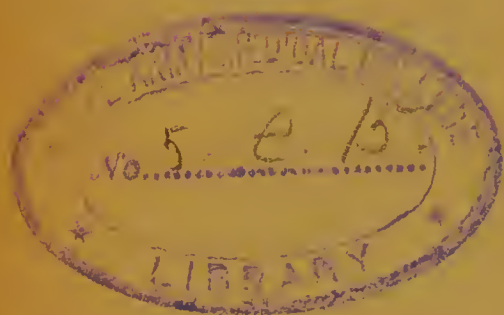


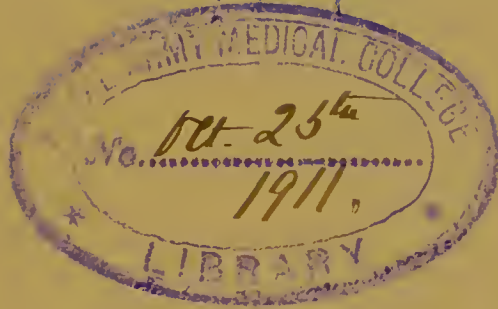
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TECHNICAL METHODS OF  
CHEMICAL ANALYSIS



# TECHNICAL METHODS OF CHEMICAL ANALYSIS

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## ENGLISH TRANSLATION

FROM THE LATEST GERMAN EDITION, ADAPTED TO ENGLISH  
CONDITIONS OF MANUFACTURE

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## PREFACE

SINCE the publication of Volume I., the preparation of a new German edition has been undertaken by Professor Lunge and Dr E. Berl, of which the two first volumes were published in 1910, and the third volume in 1911.

The sections comprised in this second volume of the English edition are included in the second and third volumes of the new German edition, which is being issued in four volumes. Advance proofs of these sections have been placed at the disposal of the Editor, so that the subject matter has been brought thoroughly up to date; this has been effected by including, in association with the additions made by the respective revisers of the English translation, all such additions as are applicable to English conditions of work that have been made in the new German edition.

The section on "Organic Dyes," from Volume IV. of the German edition, has been included in this volume, as it forms a suitable sequel to the section on "Coal Tar."

With the exception of those cases in which empirical factors are employed in technical work, all the numerical data are calculated from the table of atomic weights for 1911, issued by the International Committee, with  $O=16$  as the basis. As in Volume I., the numerical data for gases, and for the weights of substances to be taken for analysis, so as to correspond to definite volumes of gases, are calculated from the *real* litre weights according to the most reliable determinations, not from the calculated values. Also, all temperatures are given in Centigrade degrees, except where otherwise stated.

The Editor desires to record his thanks to Mr J. W. Gatehouse and

to Mr F. B. Gatehouse for assistance in the revision of the section on "Calcium Carbide and Acetylene"; to the Comptroller of His Majesty's Stationery Office for permission to reproduce the table for the correction of gas volumes from Appendix G of the "Notification of the Gas Referees for the year 1906"; and to Messrs Alexander Wright & Co., Messrs Baird & Tatlock, and Messrs Blakiston, Son & Co. of Philadelphia, for the loan of and for permission to reproduce blocks.

CHARLES A. KEANE.

LONDON, *July* 1911.



## LIST OF CONTRIBUTORS TO THE GERMAN EDITION, AND OF REVISERS OF THE ENGLISH TRANSLATION IN VOL. II.

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*Revised by* the Author.

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**Organic Dyes.**

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## LIST OF ABBREVIATED TITLES OF JOURNALS.

JOURNALS.	ABBREVIATIONS.
Acetylene . . . . .	Acetylene
American Chemical Journal . . . . .	Amer. Chem. J.
American Journal of Science . . . . .	Amer. J. Sci.
Analyst . . . . .	Analyst
Annalen der Chemie . . . . .	Annalen
Annalen der Physik . . . . .	Ann. Physik
Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie . . . . .	Ann. Chim. anal.
Annales de Chimie et de Physik . . . . .	Ann. Chim. Phys.
Archiv der Pharmacie . . . . .	Arch. Pharm.
Berg und Hüttenmännische Zeitung . . . . .	Berg u. Hütten. Zeit.
Berichte der deutschen chemischen Gesellschaft . . . . .	Ber.
Biedermann's Centralblatt für Agricultur Chemie . . . . .	Biedermann's Centr.
Bollettino chimico farmaceutico . . . . .	Boll. chim. farm.
Brewer's Journal . . . . .	Brewer's J.
British and Colonial Druggist . . . . .	Brit. and Col. Drug.
Bulletin de l'Association Belgique des Chimistes . . . . .	Bull. Assoc. Belg. des Chim.
Bulletin de l'Association chimique de Sucre et de Distillerie . . . . .	Bull. Assoc. Chim. Sucr.
Bulletin de la Société chimique de Belgique . . . . .	Bull. Soc. Chim. Belg.
Bulletin de la Société chimique de Paris . . . . .	Bull. Soc. Chim.
Bulletin de la Société Industrielle du Nord de la France . . . . .	Bull. Soc. Ind. Nord
Bulletin de la Société Industrielle de Mulhouse . . . . .	Bull. Soc. Ind. Mulhouse
Chemical News . . . . .	Chem. News
Chemical Trade Journal . . . . .	Chem. Trade J.
Chemiker Zeitung . . . . .	Chem. Zeit.
Chemiker Zeitung Repertorium . . . . .	Chem. Zeit. Rep.
Chemische Industrie . . . . .	Chem. Ind.
Chemische Revue über die Fett- und Harz-Industrie . . . . .	Chem. Rev. Fett-Ind.
Chemisches Centralblatt . . . . .	Chem. Centr.
Chemist and Druggist . . . . .	Chem. and Drug.
Comptes rendus hebdomadaires des séances de l'Académie des sciences . . . . .	Comptes rend.
Die landwirthschaftlichen Versuchs-Stationen . . . . .	Landw. Versuchs-Stat.
Dingler's polytechnisches Journal . . . . .	Dingl. polyt. J.
Electrician . . . . .	Electrician
Electrochemical and Metallurgical Industry . . . . .	Electrochem. Ind.
Engineer . . . . .	Engineer
Engineering . . . . .	Engineering
Engineering and Mining Journal . . . . .	Eng. and Min. J.
Färber-Zeitung . . . . .	Färber-Zeit.
Fischer's Jahresbericht . . . . .	Fischer's Jahresber.
Gazzetta Chimica Italiana . . . . .	Gazz. Chim. Ital.
Gerber . . . . .	Gerber

## LIST OF ABBREVIATED TITLES OF JOURNALS

JOURNALS.	ABBREVIATIONS.
Gummi-Zeitung . . . . .	Gummi-Zeit.
India-rubber Journal. . . . .	India-rubber J.
Industrie Blatt . . . . .	Ind. Bl.
Jahresbericht der Pharmazie . . . . .	Jahresber. d. Pharm.
Jahresbericht für Chemie . . . . .	Jahresber. f. Chem.
Jahresbericht der chemischen Technologie . . . . .	Jahresber. d. chem. Techn.
Journal of Analytical and Applied Chemistry . . . . .	J. Anal. and Applied Chem.
Journal de Pharmacie et de Chimie . . . . .	J. Pharm. Chim.
Journal für Gasbeleuchtung und Wasserversorgung . . . . .	J. Gasbeleucht.
Journal für praktische Chemie . . . . .	J. prakt. Chem.
Journal of Gas Lighting . . . . .	J. Gas Lighting
Journal of Physical Chemistry . . . . .	J. Phys. Chem.
Journal of the American Chemical Society . . . . .	J. Amer. Chem. Soc.
Journal of the Chemical Society . . . . .	J. Chem. Soc.
Journal of the Chemical Society, Abstracts . . . . .	J. Chem. Soc. Abstr.
Journal of the Chemical, Metallurgical, and Mining Society of South Africa . . . . .	J. Chem. Met. Soc., S. Africa
Journal of the Franklin Institute . . . . .	J. Franklin Inst.
Journal of the Institute of Brewing . . . . .	J. Inst. Brewing
Journal of the Institution of Mechanical Engineers . . . . .	J. Inst. Mech. Eng.
Journal of the Institute of Metals . . . . .	J. Inst. Metals
Journal of the Iron and Steel Institute . . . . .	J. Iron and Steel Inst.
Journal of the Physical and Chemical Society of Russia . . . . .	J. Russ. Phys. Chem. Soc.
Journal of the Royal Society of Arts . . . . .	J. Soc. Arts
Journal of the Society of Chemical Industry . . . . .	J. Soc. Chem. Ind.
Journal of the Society of Dyers and Colourists . . . . .	J. Soc. Dyers and Col.
Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Edition) . . . . .	Proc. K. Akad. Wetensch. Am- sterdam
Leather Trades Review . . . . .	Leather Tr. Rev.
Mittheilungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West . . . . .	Mitt. k. Materialprüf.
Mittheilungen aus der Centralstelle für wissenschaftlich- technische Untersuchungen . . . . .	Mitt. Centralst. Wiss.-tech. Unters.
Mittheilungen des technischen Gewerbemuseums in Wien . . . . .	Mitt. techn.-Gew. Museums
Monatshefte für Chemie der kaiserlichen Akademie der Wissenschaften, Wien . . . . .	Monatsh.
Monatsschrift für Textil-Industrie . . . . .	Monatsschrift, f. Text.-Ind.
Moniteur Scientifique . . . . .	Monit. Scient.
Oesterreichische Chemiker Zeitung . . . . .	Oesterr. Chem. Zeit.
Paper and Pulp . . . . .	Paper and Pulp
Papier-Zeitung . . . . .	Papier-Zeit.
Petroleum Review . . . . .	Petrol. Rev.
Pharmaceutical Journal . . . . .	Pharm. J.
Pharmaceutical Review . . . . .	Pharm. Rev.
Pharmaceutisches Centralblatt . . . . .	Pharm. Centr.
Pharmazeutisch Weekblad . . . . .	Pharm. Weekblad
Pharmazeutische Zeitung . . . . .	Pharm. Zeit.
Philosophical Magazine and Journal of Science . . . . .	Phil. Mag.
Philosophical Transactions of the Royal Society . . . . .	Phil. Trans.
Proceedings of the American Academy . . . . .	Proc. Amer. Acad.
Proceedings of the American Electrochemical Society . . . . .	Proc. Amer. Electrochem. Soc.
Proceedings of the American Institute of Mining Engineers, and also Bulletin . . . . .	Proc. Amer. Inst. Min. Eng.; Bull. Amer. Inst. Min. Eng.

## JOURNALS.

## ABBREVIATIONS.

Proceedings of the Faraday Society . . . . .	Proc. Faraday Soc.
Proceedings of the Institution of Civil Engineers . . .	Proc. Inst. Civ. Eng.
Proceedings of the Institution of Mining and Metallurgy .	Proc. Inst. Min. and Met.
Proceedings of the Royal Society . . . . .	Roy. Soc. Proc.
Revue Générale des Matières Colorantes . . . . .	Rev. Gen. Mat. Col.
Revue internationale des Falsifications . . . . .	Rev. intern. Falsif.
Receuil des travaux chimiques des Pays-Bas et de la Belgique . . . . .	Rec. trav. chin.
Scientific American . . . . .	Scient. Amer.
Stahl und Eisen . . . . .	Stahl u. Eisen
Tonindustrie Zeitung . . . . .	Tonindustrie Zeit.
Transactions of the Institute of Mining and Metallurgy .	Trans. Inst. Min. and Met.
United States Consular Reports . . . . .	U.S. Cons. Reps.
Zeitschrift der analytischen Chemie . . . . .	Z. anal. Chem.
Zeitschrift für angewandte Chemie . . . . .	Z. angew. Chem.
Zeitschrift der anorganischen Chemie . . . . .	Z. anorg. Chem.
Zeitschrift des Vereins der deutschen Zucker-Industrie .	Z. Ver. deut. Zuckerind.
Zeitschrift des Vereins für deutsche Ingenieure . . .	Z. Verein. deutsch. Ingen.
Zeitschrift für chemische Apparatenkunde . . . . .	Z. für chem. Apparatenkunde
Zeitschrift für das gesammte Brauwesen . . . . .	Z. ges. Brauw.
Zeitschrift für Elektrochemie . . . . .	Z. Elektrochem.
Zeitschrift für Farben Industrie . . . . .	Z. Farb. Ind.
Zeitschrift für physikalische Chemie . . . . .	Z. physik. Chem.
Zeitschrift für Spiritusindustrie . . . . .	Z. Spiritusind.
Zeitschrift für Untersuchung der Nahrungs-und Genuss- mittel . . . . .	Z. Unters. Nahr. u. Genussm.
Zeitschrift für Zuckerindustrie in Böhmen . . . . .	Z. Zuckerind. Böhm.
West Indian Bulletin . . . . .	West Ind. Bull.
Wochenschrift für Brauerei . . . . .	Woch. f. Brau.



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## IRON

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THE manufacture of iron may be divided into two main branches—viz., the preparation of pig iron by blast furnace smelting, and its conversion into malleable iron by refining.

The raw materials of the former process are iron and manganese ores, fluxes, and fuels, whilst the main products are iron, slag, and furnace gases. In the refining processes, pig iron is practically the sole raw material, though fluxes are occasionally added ; the products are numerous varieties of malleable iron and slag.

Iron ores include not only naturally occurring ferruginous and manganiferous minerals, but also certain industrial by-products, such as refinery slag, rolling-mill scale, pyrites, cinders, etc. Fluxes are almost invariably carbonates of the alkaline earths. In regard to fuels, their value, apart from calorific effect, is determined chiefly by the composition of the ash. Slags are always silicates, sometimes mixed with considerable amounts of ferroso-ferric oxide and of phosphates.

The analytical investigation of ores, fluxes, fuel ashes, and slags is similar in character, so that they may be treated as a single group. Also, all varieties of iron and steel, excepting those alloyed with rare metals, contain the same constituents. Hence the subject matter of this section divides itself into two groups—the analysis of ores and the analysis of iron.

### I.—ANALYSIS OF ORES

#### A. QUALITATIVE TESTS

The naturally occurring iron ores are mainly ferric oxide (red hæmatite), ferroso-ferric oxide (magnetic ore), hydrated oxide (brown



hæmatite), or carbonates (spathic iron ore, clay-ironstone); the natural silicates (chamosite, knebelite) and chrome iron ore are less common. The industrial residues worked up as ores are oxides (pyrites cinder), silicates mixed with much ferroso-ferric oxide (refinery slag), or the latter alone (mill and forge scale).

All these materials contain iron as the chief constituent, as a matter of course, but it may be desirable to test for the presence of one or both stages of oxidation. The natural ores are never quite pure, but always contain foreign matter or are permeated with other minerals, so that they usually contain silica, alumina, lime, baryta, magnesia, and more rarely alkalis. The usual tests are applicable for their detection, as is also the case with the recognition of the presence of water and of organic matter; the latter is an invariable constituent of clay-ironstone.

Apart from the iron content, an ore is rendered more or less valuable by the presence or absence of certain other constituents. Manganese, on the one hand, often increases its value; such impurities as phosphates, sulphates, sulphur, copper, lead, zinc, antimony, arsenic, and titanium, on the other hand, may depreciate it considerably. It is accordingly important to test for these substances. Occasionally the more or less comparatively rare elements, such as cobalt, nickel, chromium, etc., may have to be looked for.

The presence of water, either as moisture or in chemical combination, of organic matter, and of carbonic acid, frequently affords information as to the variety of ore under examination.

**Manganese.**—A little powdered ore is fused with six parts of sodium carbonate and a pinch of nitre on a platinum foil; if manganese be present, the melt is coloured green. This is an exceedingly delicate reaction.

**Phosphoric Acid.**—A warm nitric acid solution of the ore is added, drop by drop, to an equal volume of nitro-molybdate reagent, heated to  $40^{\circ}$  to  $50^{\circ}$ , and the mixture thoroughly shaken for from five to ten minutes, when the yellow precipitate of phospho-molybdate of ammonia will be formed; if the phosphoric acid is only present in traces, the solution must be kept at  $40^{\circ}$  to  $50^{\circ}$  for an hour or more for the precipitate to settle out.

The molybdate solution is prepared by dissolving 150 g. of pure ammonium molybdate in water, 450 g. of ammonium nitrate are added to the solution, the whole diluted to 1000 c.c., poured into 1000 c.c. of nitric acid of sp. gr. 1.19, allowed to stand for twenty-four hours at  $35^{\circ}$ , and filtered.

Hæmatites for the Bessemer acid process, spathic ores, and magnetic ores, are often almost free from phosphoric acid; in these cases it is well to take several grams for the test and to concentrate the solution.

**Sulphuric Acid** is tested for by the ordinary blowpipe reaction for sulphur.

**Sulphur.**—To test for sulphides, decomposition by acid may be employed, or the ore may be mixed with sodium carbonate and borax and heated in the blowpipe on charcoal, when sodium sulphide will be formed.

**Lead.**—A hydrochloric acid solution of the ore is concentrated, with the addition of sulphuric acid, in a porcelain dish, and a third of its volume of alcohol added. On pouring the liquid into a small beaker, any precipitate of lead sulphate will be at once recognised. To make sure that it is not barium sulphate, the precipitate, after thorough washing, should be tested with ammonium sulphide; or, it may be dissolved in a warm, ammoniacal solution of ammonium acetate, and tested with potassium chromate.

**Copper.**—The ore is dissolved in strong hydrochloric acid and the solution concentrated; a thick platinum wire is then dipped into the solution and held in a Bunsen flame, when copper will give a green coloration. For very minute quantities of copper, it is better to precipitate from acid solution, at  $70^{\circ}$ , with sulphuretted hydrogen, and to test the precipitate either in a borax bead or otherwise.

**Zinc.**—Ores containing zinc, when heated in the blowpipe on charcoal with sodium carbonate, give an incrustation, yellow when hot and white when cold, which assumes a fine green tint, most vivid in the cold, on addition of cobalt nitrate. For mere traces of zinc, it is best to employ the method given on p. 19.

**Antimony.**—A sample of the finely powdered ore is dissolved in aqua regia and repeatedly evaporated with hydrochloric acid to expel the nitric acid; the residue is then taken up with a little hydrochloric acid and the solution placed on the lid of a platinum crucible, together with a piece of zinc. The least traces of antimony produce a brown stain. Larger amounts may be recognised by the white incrustation, which is formed in the blowpipe test; this incrustation disappears when blown upon.

**Arsenic** also yields a white incrustation in the blowpipe test, but it settles at a greater distance from the substance, and is much more volatile than that of antimony; at the same time, a strong alliaceous odour, due to arsenious oxide, is evolved. Very small quantities of arsenic, especially if present as arsenate, are best determined quantitatively, as described subsequently (p. 20).

**Cobalt and Nickel.**—A solution of the ore in hydrochloric acid is precipitated with ammonia and ammonium sulphide, the precipitate extracted with very dilute hydrochloric acid, and the black residue, if any, fused in a borax bead in the oxidising flame. Cobalt yields a blue bead, nickel a reddish yellow bead which turns pale yellow on cooling.

A very delicate test for nickel consists in treating a dilute ammoniacal solution of the ore with an excess of tartaric acid and an alcoholic solution of dimethylglyoxime, when a bright red crystalline precipitate is formed in presence of nickel; cobalt gives no reaction with this reagent (*cf.* p. 66).

**Chromium.**—Minute traces are best detected by the blue ethereal solution of perchromic acid obtained on treating an acid solution of chromic acid with hydrogen peroxide. Larger quantities, when tested in borax or microcosmic salt beads, give a green coloration, more pronounced in the cold than when hot. To carry out the perchromic acid test the finely powdered ore is fused with a mixture of six parts of sodium carbonate and one part of potassium chlorate, the melt extracted with water, and the solution acidified with sulphuric acid. A few cubic centimetres of hydrogen peroxide and of ether are placed in a test tube and the solution added in small portions with frequent shaking. In presence of chromium, the ethereal layer will be coloured blue. The test is vitiated by the presence of vanadium, which would impart a red colour to the ether. Another test is to acidify the extract of the melt with acetic acid and to add lead acetate, when a yellow precipitate of lead chromate is formed.

**Titanium.**—A fairly large sample of the ore is fused with fifteen parts of acid potassium sulphate, the melt allowed to cool, dissolved in cold water, the silica filtered off, and the clear liquid placed in a large test tube with a piece of zinc; if titanium be present, the solution becomes violet coloured after a short time. Or, a little of the finely powdered ore is dissolved in a microcosmic salt bead by prolonged ignition over the blowpipe; titanium imparts a yellow coloration, which turns violet when cold. This test fails when other metals, such as cobalt, etc., are present, in which case the titanous acid is first separated as follows:—The extract of the acid sulphate melt is treated with sulphuretted hydrogen to reduce ferric salts, and then boiled for some time in a current of carbon dioxide; any precipitate formed is filtered off and dissolved in the microcosmic salt bead, which is coloured as above in the reducing flame; heated in the oxidising flame, the bead becomes colourless. Titanous acid containing iron gives a brownish red bead in the reducing flame.

**Vanadium.**—There is never sufficient vanadium in iron ores to give the blowpipe test. One to two grams of the ore are fused with sodium carbonate and nitre, the melt extracted with hot water, the filtered solution acidified somewhat strongly with sulphuric acid and treated with sulphuretted hydrogen. A coloration varying from yellowish red to deep red, according to the amount of vanadium present, results.



## B. QUANTITATIVE ANALYSIS

Full and detailed analyses of ores, fluxes, and slags are rarely required in iron-works. As a rule, such analyses are only carried out upon average samples of the various materials at fairly long intervals, either for calculating the blast furnace charges or for controlling the correctness of the calculations by analyses of the slag, or when it is a question of the purchase of ores. In the majority of cases, as, for instance, for controlling the quality of regular consignments of ore, it suffices to determine the chief valuable and injurious constituents—viz., iron, manganese, phosphorus, sulphur, copper, zinc, and silica. Frequently it is not necessary to determine more than the iron, manganese, and insoluble residue. Volumetric methods are, of course, used whenever possible in works' laboratories. Gravimetric methods will, however, be considered first, because the separations, etc., involved in these have often to be carried out before the volumetric methods can be applied.

**Sampling** (*cf.* Vol. I., pp. 7-17).—Gravimetric or volumetric analyses cannot lead to results which are of practical value and do justice to both buyer and seller, unless the sample handed to the chemist really represents an average of the bulk from which it was drawn. It is often a matter of great difficulty, requiring considerable preliminary operations, to secure this. The more finely divided and homogeneous the ore is, the easier is the sampling. In such cases it suffices to take 1 to 2 kg. of ore from each truck-load, collect the whole in a large box, and draw an average sample from the latter at intervals of, say, a week, or else after a certain number of truck-loads, as agreed upon, have been delivered. Should the material, however, be in large lumps (*e.g.*, fluxes, Spanish hæmatite, Swedish magnetic ore), it is much more difficult to draw a genuine average sample, since the lumps are apt to vary greatly in composition. In this case the best course is to come to an agreement with the vendor that a certain truck-load, already under way, shall be considered as representative of the whole consignment or ship-load. On arrival, this truck-load is comminuted separately by means of a stone-breaker, or, better, a roller-mill, and an average sample is drawn from the resulting heap.

This is effected as follows:—The material is placed on a tiled floor and spread out in a circle; starting from the circumference, it is then shovelled towards the centre until it is heaped in a cone. The cone is broken up, the material again spread out, and the operation repeated. After three such mixings, the evenly spread mass is divided into four quadrants, and two opposite quadrants, or one only, are taken aside, mixed, and again divided; and so on, until a quantity of only 1 to 2 kg. remains. This is then ground up in an iron mortar in the laboratory,

and further divided as above, so that a sample suitable for analysis is finally obtained.

The sample is prepared in triplicate: one portion is analysed, the second delivered to the vendor, and the third sealed and kept in case of disputes.

The size of grain should not exceed:—

For a:—	100 g. sample	0.5 mm. diameter.
„ 100 to 500 g.	„ 1	„ „
„ 500 „ 1000 g.	„ 2	„ „
„ 1000 „ 2000 g.	„ 3	„ „

The sample for analysis must be ground down to pass a sieve of about 0.5 mm. mesh before being weighed out. In the case of clay-ironstones and calcareous ores, the samples must be finely powdered in an agate mortar to render them uniform.

Various mechanical sampling contrivances have been designed, but they have not found much favour in works' practice.

## I. GRAVIMETRIC ANALYSIS

**Weighing Out.**—When the sample is not homogeneous in grain, it often happens that a partial separation of the lighter and heavier portions takes place when the scoop or spatula, from which the substance is weighed out, is tapped. Hofmann<sup>1</sup> has pointed out that analytical discrepancies are sometimes due to this. Iron ores which are not finely powdered are likely to behave in this way, and in such cases it is preferable to weigh out a tolerably large portion of the sample, to then dissolve the whole and to take an aliquot portion of the solution for analysis.

**Water or Loss on Ignition.**—As a rule, it is merely necessary to determine the moisture, which is expelled by drying a fresh sample of the ore in the air-oven. For red hæmatites the best temperature is 110°, for brown hæmatites rich in manganese 100°, and for soft peaty ores 90°. If, in addition, it is required to determine the combined water, as in brown hæmatites, the sample is further gradually brought to a red heat and ignited to constant weight; if carbonates or ferrous compounds be present, however, this method cannot be used, and the expelled water must be collected and weighed in a calcium chloride tube or other suitable absorbent. For this purpose, 1 g. of the finely powdered ore is placed in a boat and ignited in a combustion tube in a current of dried air; care must be taken to dry the air with the same substance (calcium chloride, sulphuric acid, phosphoric acid) as is used in the absorption tube.

<sup>1</sup> *Z. angew. Chem.*, 1891, 4, 440.

In the presence of organic matter, as is invariably the case with bog-ores, it is customary to determine the loss on ignition which comprises the water, carbonic acid, and organic matter ; if the percentage of ferrous and ferric iron be known, the proportion of slag-forming constituents can then be calculated.

The presence of organic matter also necessitates a preliminary ignition of the sample, previous to solution, unless volatile constituents such as arsenic, sulphur, or carbonic acid are present ; the weighed ore is ignited, at not too high a temperature, in an open porcelain crucible until the organic matter is destroyed.

**Dissolving the Ore.**—The best solvent is fuming hydrochloric acid (sp. gr. 1.19), which is allowed to act on the finely powdered ore in an Erlenmeyer flask at 50°, the temperature being ultimately raised to the boiling point. The flask is most suitably warmed on a sand-bath or on a heated iron plate. In order to obtain all the iron in the ferric state, as is necessary for many gravimetric and volumetric methods, a little nitric acid or potassium chlorate is added when the solution is nearing completion. In case it is preferable to dissolve in sulphuric acid, dilute acid (1 to 1 by volume) is employed and the temperature kept at 100°.

If the undissolved residue is not white, but more or less coloured, the iron is extracted from it by one of the following methods:—Either the residue is fused with sodium and potassium carbonates, or else it is dried, moistened in a platinum crucible with hydrofluoric and sulphuric acids, evaporated, and finally dissolved, the solution being added to the main bulk.

The solution of ores in sulphuric acid is greatly facilitated by previous reduction to the metallic state, which may be effected by hydrogen or coal gas, or by certain powdered metals. In the former case, the weighed substance is placed in a boat or on a piece of copper foil in a combustion tube held in an ordinary clamp. The gas is passed through at such a rate that a small flame continues to burn at the exit, whilst the tube is heated to redness by means of one or two burners ; the reaction is completed after ten to fifteen minutes. The substance is then allowed to cool in a current of the gas and immediately dissolved in sulphuric acid (1 : 3).

In the second method, which is due to Donath and Jeller,<sup>1</sup> the finely powdered ore is mixed with an approximately equal volume of zinc dust in a porcelain crucible, covered with a layer of the same, and strongly ignited for from five to eight minutes with the lid on. The reaction is so vigorous that incandescence of the mixture, which may be observed through the walls of the crucible, sets in. In order that the reduction may be complete, ores containing ferrous iron must previously be moistened with ammonium nitrate and ignited, so as to oxidise all

<sup>1</sup> *Z. anal. Chem.*, 1886, 25, 361 ; *Chem. News*, 1886, 54, 73.



the iron to the ferric state. It is, of course, necessary to make a blank determination of iron in the zinc dust.

V. Jüptner<sup>1</sup> uses magnesium powder instead of zinc; for complete reduction four to six parts are mixed with one part of a comparatively refractory ore. In the case of easily reducible ores and slags, poor in iron, it suffices to mix the sample with an equal volume of magnesium, then to add a layer of as much magnesium again in the crucible, and to ignite cautiously for five to ten minutes. A blank determination of the iron in the magnesium is also necessary in this case.

**Insoluble Residue and Silica.**—When ores of known quality are being smelted, all that is usually required by way of control is the determination of the insoluble residue (silica, quartzose sand, barytes, clay, and undecomposed mineral admixtures) and of the iron. For this purpose the solution, prepared as above, is diluted and filtered, and the residue ignited over the blast in a platinum crucible and weighed. To determine the silica, the solution is twice evaporated to dryness, taken up with acid, diluted with water, heated, and the residue filtered and ignited. In evaporating, it is well to avoid excessive heating, since basic chlorides or ferric hydroxide, which redissolve with difficulty, tend to separate out. Moreover, ferric chloride is markedly volatile at comparatively low temperatures, which may lead to low results in the subsequent determination of the iron. Since the silica thus obtained is never pure, the contents of the crucible, after weighing, should be evaporated with hydrofluoric and sulphuric acids, strongly ignited and re-weighed. The loss in weight represents the pure silica.

Should the residue contain barytes, clay, or undecomposed ore, it must be fused with sodium and potassium carbonates, and the melt dissolved in warm water without the addition of acid. This is facilitated by first removing it from the crucible; the solidified mass is heated until the outer layer just melts, when it can be got out without difficulty by pressing the sides of the crucible.

The following is the procedure adopted by C. B. Murray,<sup>2</sup> of the American Steel Trust Laboratories, for the determination of silica in iron ores. One gram of the finely ground and dried ore is thoroughly fused with 12 to 15 g. of sodium carbonate. The melt is cooled and extracted in a beaker containing 200 c.c. of water, to which the same volume of strong hydrochloric acid is subsequently added. The solution of the melt is then evaporated to dryness, the residue taken up with 50 c.c. of hydrochloric acid, diluted with water, and the silica filtered off, ignited, and weighed.

In the case of manganese ores, the following modification is adopted. One gram of the ore is dissolved in 50 c.c. of hydrochloric acid, the

<sup>1</sup> *Chem. Zeit.*, 1894, **20**, 469; *J. Iron and Steel Inst.*, 1894, ii., 497.

<sup>2</sup> *Methods of Iron Analysis*, p. 50 (see Literature, p. 89).

solution boiled and filtered and the residue fused and added to the original solution; the whole is then treated as above. The action of the liberated chlorine on the crucible is thus avoided.

**Iron and Aluminium.**—Iron is hardly ever determined gravimetrically; even when both ferrous and ferric iron are present, volumetric methods are employed. When aluminium, however, has to be determined, ferric and aluminium hydroxides are precipitated jointly from acid solution by a slight excess of ammonia and weighed together. The very general method of using a large excess of ammonia and then boiling it off is not to be recommended, because it is by no means easy to judge the point of neutrality; if boiling be continued beyond this point, some ammonium chloride is apt to be dissociated and an equivalent amount of alumina brought into solution again, as has been shown both by Blum<sup>1</sup> and by Lunge.<sup>2</sup> It is preferable to precipitate with a small excess of ammonia, add ammonium chloride if necessary, allow to settle, and filter at once. The ignited and weighed precipitate, which contains all the phosphoric acid present as well as the oxides, is fused with acid potassium sulphate and the iron determined volumetrically. The aluminium may then be found by difference, after the phosphoric acid has been separately determined. In order to determine alumina as such, the separation from iron may be carried out by pouring the hot solution of the joint precipitate, which should not be too dilute, into boiling sodium hydroxide, preferably contained in a platinum dish. The diluted liquid is then filtered, the filtrate acidified, and the alumina precipitated with a slight excess of ammonia. The precipitate must be redissolved and reprecipitated, in order to free it from fixed alkali; it will contain all the phosphoric acid, which must also be determined and deducted in this case.

This separation is greatly facilitated by the ether-extraction method proposed by Rothe,<sup>3</sup> which is specially adapted to the separation of large quantities of iron from small quantities of manganese, chromium, nickel, aluminium, copper, cobalt, vanadium, and titanium. It is based on the fact that ferric chloride in presence of hydrochloric acid and ether gives a compound which is easily soluble in the latter, whereas the chlorides of the other metals enumerated do not possess this property. Hence it is possible to extract ferric chloride quantitatively by means of ether and so to remove heavy "ballasts" of iron. The essential conditions for carrying out this method are—(1) that the iron be present as ferric chloride; (2) that an excess of acid of definite strength be present; and (3) that there be no superfluous water.

Five grams of the ore are dissolved in hydrochloric acid and the

<sup>1</sup> *Z. anal. Chem.*, 1888, 27, 19.

<sup>2</sup> *Z. angew. Chem.*, 1889, 2, 634; *J. Soc. Chem. Ind.*, 1890, 9, III.

<sup>3</sup> *Cf. Chem. News*, 1896, 74, 296.



solution filtered ; the washed residue is then fused, the silica removed, and the alumina precipitated in the filtrate by ammonia. If this precipitate contains iron, it is dissolved in hydrochloric acid and added to the bulk. The solution is then oxidised, if necessary, by adding a few drops of

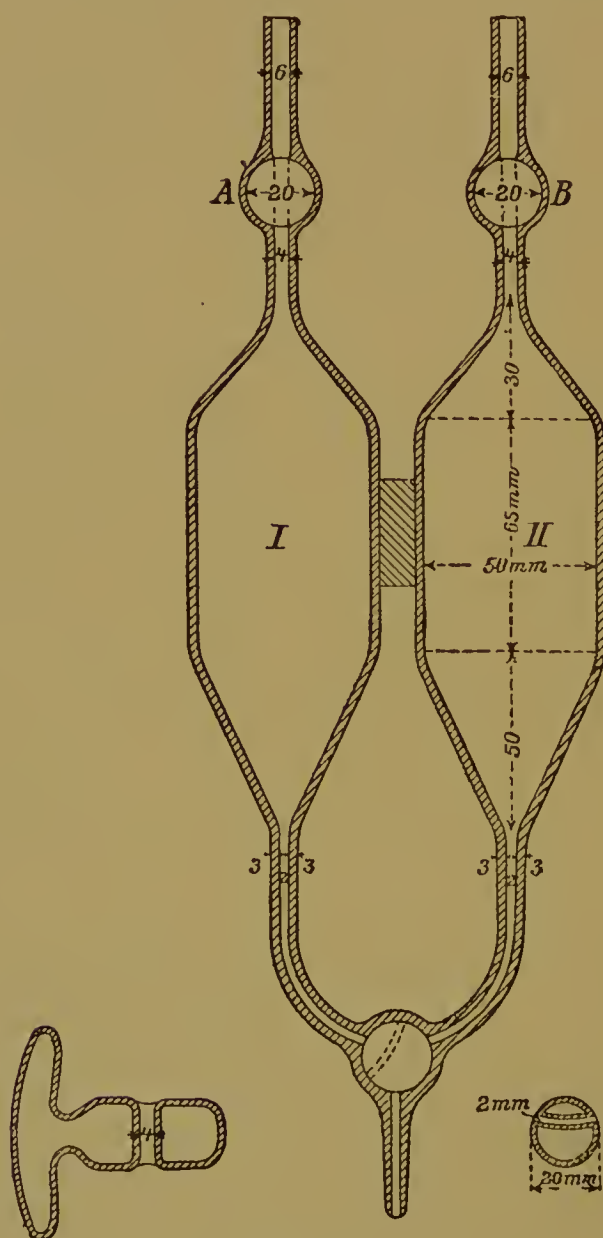


FIG. 1.

strong nitric acid, concentrated to about 10 c.c., poured through an elongated funnel into one limb of the Rothe separator (Fig. 1), and rinsed with hydrochloric acid of sp. gr. 1.124 (at 19°), until the total volume reaches 55 to 60 c.c. It is important that the solution should be quite clear and free from basic precipitates. The cylindrical limbs of the separator are fitted with stopcocks at the top and are connected

at the bottom by a three-way stopcock. The apparatus is held in a clamp when in use.

The solution having been charged, say, into limb II, an equal volume of ether is poured into limb I, which is placed under pressure by means of a piece of rubber tubing attached to the mouth; the tubes I and II are then connected by turning the three-way stopcock and the ether driven over into II. All the taps are then closed, the liquids brought into contact by thorough shaking, the apparatus allowed to stand until the layers have completely separated, and the lower layer driven into I as before. The upper ethereal layer is then run off by means of the three-way stopcock. A fresh supply of ether is poured into the now empty limb II and the extraction repeated. Ledebur recommends an ordinary separating funnel in place of the Rothe separator.

The solution, which is now deprived of iron, is evaporated to dryness, taken up with hot water and a few drops of hydrochloric acid, and heated to boiling, after the addition of 1 c.c. of concentrated acetic acid and 1 g. of sodium acetate; 2 c.c. of a saturated solution of sodium phosphate are then added to precipitate the aluminium. The precipitate, which, even after washing with hot water, is apt to retain manganese and copper, is redissolved in a little hydrochloric acid, evaporated to dryness, taken up with a few cubic centimetres of water, boiled for some time with 2 or 3 g. of aluminium-free sodium hydroxide, made up to 250 c.c., and filtered through a dry filter paper. Two hundred c.c. of the filtrate, corresponding to 4 g. of ore, are acidified with acetic acid and the aluminium precipitated as phosphate. The well washed precipitate is ignited, and then contains 41.85 per cent. of  $\text{Al}_2\text{O}_3$ .

According to A. Wencélius,<sup>1</sup> aluminium can be determined directly in the solution of the ore, provided barium and strontium salts soluble in hydrochloric acid, and titanous acid are absent; it is precipitated as phosphate in acetic acid solution after the previous reduction of ferric to ferrous salts by sodium hyposulphite.

**Manganese.**—In works' laboratories manganese is generally determined volumetrically, especially if the ore is to be assayed for manganese or for manganese and iron only. In conducting a complete analysis, however, a gravimetric determination will be found more suitable; this necessitates the previous removal of the iron and aluminium. The following five methods are available for this separation:—

**Separation of Manganese from Iron and Aluminium.**—I. *Acetate Method.* The oxidised solution in hydrochloric acid of 1 to 2 g. of the ore (or more if the content of manganese be very low) is evaporated

<sup>1</sup> *Analytische Methoden für Thomas-Stahlhütten Laboratorien.*

to dryness, redissolved in the least possible quantity of hot hydrochloric acid, allowed to cool, diluted with cold water, heated nearly to boiling, and filtered. The completely cooled filtrate, the bulk of which should not exceed 250 c.c., is then accurately neutralised with ammonium carbonate; if a permanent precipitate is formed, owing to the addition of an excess of this reagent, it is redissolved in hydrochloric acid and the neutralisation continued. It is convenient to have a strong and a dilute solution of ammonium carbonate and to use the latter towards the end of the process; in the earlier stages, solid powdered ammonium carbonate may be used with advantage. About 0.75 g. of ammonium acetate for each gram of iron taken is then added to the deep red solution, the volume of which is made up to about 1000 c.c. by the addition of boiling water, and the whole placed on a hot plate and boiled for one or two minutes. Long-continued boiling renders the precipitate slimy and difficult to filter. In many works' laboratories the sodium salts are preferred: a more complete separation is thereby effected (Lambert).

The precipitated basic ferric acetate is allowed to settle, the colourless solution decanted off through a large filter, and the precipitate washed by decantation with hot water in which a little ammonium acetate is dissolved. The precipitate contains all the aluminium and phosphoric acid present, in addition to the iron; it can be used for the volumetric determination of the iron.

If the neutralisation, which requires some little practice and patience, has been properly carried out, a single separation may suffice. If special accuracy, however, is required, or in case of lack of experience with the method, it is desirable to redissolve the iron precipitate, repeat the separation, and unite the filtrates. The precipitate may be tested for manganese by dissolving it in nitric acid and boiling with lead peroxide or bismuth tetroxide, or other oxidising agent, which yields a pink coloration in presence of manganese. A preliminary examination of the lead peroxide, which frequently contains manganese, must be made; for this purpose a sample is dissolved in hot concentrated sulphuric acid, diluted, allowed to cool, and treated with a further portion of the peroxide, when no pink colour should be formed.

The voluminous basic acetates of iron and aluminium are difficult to wash, and are apt to pass through the filter towards the end of the filtration. Washing may be entirely circumvented by resorting to the method of partial filtration, which is carried out as follows:—The precipitation is effected in a large pear-shaped flask, in which the solution, diluted to not quite 1000 c.c., is heated directly by a large burner, without any interposed wire gauze. There is no fear of the flask cracking if it has once stood the heating. After adding the precipitant

and boiling briskly for half a minute, the contents are poured into a litre flask and made up with boiling water; or else the volume is read off by means of marks placed at intervals of 1 c.c. on either side of the litre mark. The solution is then filtered through a large pleated filter paper until 750 c.c. have been collected, the operation being so rapidly performed that the liquid is not cooled down by more than a few degrees. The filtrate is used for the determination of the manganese, the residual liquid and precipitate being discarded.

For specially accurate work, it is desirable to take into account the fall in temperature and also the volume of the precipitate. Corrections for the former may be made by the aid of the subjoined table;<sup>1</sup> the precipitate may be assumed to displace 0.7 c.c. for every 1 g. of iron.

100°	95°	90°	85°	80°	75°	70°	65°	60°	55°	50°	45°
100.00	100.37	100.72	101.07	101.40	101.71	102.02	102.31	102.63	102.84	103.08	103.30
...	100.00	100.36	100.69	101.02	101.33	101.64	101.93	102.21	102.46	102.70	102.91
...	...	100.00	100.34	100.64	100.97	101.24	101.57	101.85	102.10	102.33	102.56
...	...	...	100.00	100.32	100.63	100.94	101.20	101.50	101.75	101.98	102.21
...	...	...	...	100.00	100.30	100.62	100.90	101.17	101.42	101.62	101.88
...	...	...	...	...	100.00	100.30	100.59	100.86	101.11	101.34	101.57
...	...	...	...	...	...	100.00	100.28	100.55	100.80	101.03	101.26
...	...	...	...	...	...	...	100.00	100.27	100.51	100.74	100.97
...	...	...	...	...	...	...	...	100.00	100.24	100.47	100.70
...	...	...	...	...	...	...	...	...	100.00	100.23	100.45
...	...	...	...	...	...	...	...	...	...	100.00	100.22

2. *Ammonium Carbonate Method.* The oxidised solution of the ore in hydrochloric acid is evaporated to dryness, which can be done in a beaker upon a sand-bath, or in a dish over a wire gauze, and the residue is taken up with hot water and slightly acidified. About 5 g. of ammonium chloride for every 1 g. of ore are then added, together with at least 250 c.c. of water per gram of ore. The solution is neutralised with dilute ammonium carbonate solution, which is added until the liquid just begins to become turbid; should a permanent precipitate be formed, a few drops of acetic acid are added and the solution allowed to stand until it becomes clear. On heating to boiling, and continuing to boil until all the carbon dioxide has been driven off, a precipitate of basic iron and aluminium salts, which settles readily, is formed. This is somewhat difficult to wash, and may therefore be separated by partial filtration, as described above. If the supernatant liquid is not colourless, but slightly yellow, the iron has not been completely precipitated, and a few drops of ammonia must be added before filtering, but not enough to be noticeable by the smell.

The filtrate should be faintly acid and colourless; it is acidified

<sup>1</sup> Cf. *Z. angew. Chem.*, 1888, **1**, 220; also H. Bracley and F. Ibbotson, *The Analysis of Steel Works Materials*, p. 31.



slightly to keep the manganese in solution, boiled down to a small bulk, and a few drops of ammonia added, any ferric or aluminium hydroxide which is precipitated being filtered off and tested for traces of manganese. The determination of the manganese in bulk is then proceeded with by the usual methods.

3. *Sulphate Method.* The chief advantage of this method, which is due to Kessler,<sup>1</sup> is that the precipitate is easily washed. The oxidised hydrochloric acid solution is approximately neutralised with ammonia, and ammonium carbonate added to incipient turbidity. So long as the liquid is dark brown and of acid reaction, no precipitation of manganese need be feared. One gram of ammonium sulphate for every gram of iron is then added to the cold solution, when a brown precipitate of basic ferric sulphate is formed. Should the precipitate be of comparatively light colour, it indicates that the neutralisation was incomplete and that iron has remained in solution. The precipitate is very bulky, and filters with difficulty at first, but gives no trouble in washing. The aluminium remains partially in the filtrate, but can be removed by adding a few drops of ammonium acetate and boiling. Partial filtration, as described above, is also useful in this method.

4. *Zinc Oxide Method.*<sup>2</sup> One to two grams of iron ore, or 0.5 g. of manganese ore, is dissolved in hydrochloric acid, filtered, oxidised with potassium chlorate or hydrogen peroxide, boiled till free from chlorine, and diluted to 400 or 800 c.c. in a measuring cylinder, according to the amount of iron present. Zinc oxide, finely powdered and suspended in water, is then added in small quantities at a time with thorough agitation, until the precipitated ferric hydroxide suddenly coagulates. On settling, the liquid will be found to be colourless. It is made up to a known volume, shaken, and subjected to partial filtration.

C. B. Murray<sup>3</sup> adopts the following procedure when using this method for the estimation of manganese in the case of manganiferous iron ores. One gram of the ore is dissolved in 50 c.c. of hydrochloric acid, evaporated to dryness, the residue taken up with 20 c.c. of nitric acid, and again evaporated to about 10 c.c. The solution is then washed into a 500 c.c. flask, diluted to about 200 c.c., and zinc oxide, suspended in water, added till all the iron is precipitated. The whole is diluted to 500 c.c., acidified, thoroughly shaken, allowed to settle, and 250 c.c. of the clear solution decanted off into a flask. This solution is then boiled for about five minutes and titrated with a standard solution of potassium permanganate.

5. *Ether Method.* Rothe's method for separating iron from

<sup>1</sup> *Z. anal. Chem.*, 1872, 11, 258; *J. Iron and Steel Inst.*, 1880, 353; *Iron*, May 31, 1879.

<sup>2</sup> *Cf. Volhard, Chem. News*, 1879, 40, 207; *J. Iron and Steel Inst.*, 1880, p. 355.

<sup>3</sup> *Methods of Iron Analysis*, p. 53 (see Literature, p. 89).



aluminium, described on p. 9, is sometimes employed with advantage for separating iron from manganese.

**Determination of Manganese.**—I. *Manganese Peroxide Method.* To precipitate manganese as hydrated peroxide, bromine, bromine water, brominated air, or hydrogen peroxide may be used. The iron-free filtrate is nearly neutralised with ammonia or sodium carbonate, evaporated down to about 250 c.c., cooled to 50°, and treated with so much bromine or bromine water that the liquid retains a deep yellow colour. On heating the solution to the boiling point, the colour will disappear; more bromine is then added, and the process repeated until a distinct permanganate colour is obtained. The permanganate is then reduced with a few drops of alcohol, the precipitate of manganese peroxide filtered off, washed with dilute hydrochloric acid (1 per cent. by volume) and with water, and finally ignited to  $\text{Mn}_3\text{O}_4$ . Should the quantity of the precipitate be very considerable, it is well to char the filter gently before proceeding to full ignition.

If the precipitation has been carried out in the presence of alkali salts, such as sodium acetate or carbonate, the peroxide will usually be contaminated with these, and should be redissolved in hydrochloric acid and reprecipitated with sodium carbonate; the manganese carbonate is washed well and ignited to  $\text{Mn}_3\text{O}_4$ . In this operation some manganese is apt to remain in the filtrate and washings; it can be recovered by evaporating to dryness and taking up with water; the amount, however, is generally negligible.

The precipitation of manganese peroxide is very conveniently carried out by Wolff's method,<sup>1</sup> preferably by means of the apparatus shown in Fig. 2. A current of air is propelled by a blower, or drawn by a filter-pump, through the flask *a*, which contains bromine water with some pure bromine at the bottom, and thence into a large conical flask, *d*, in which the filtrate containing the manganese is placed; this filtrate is not previously concentrated, but is made strongly ammoniacal.

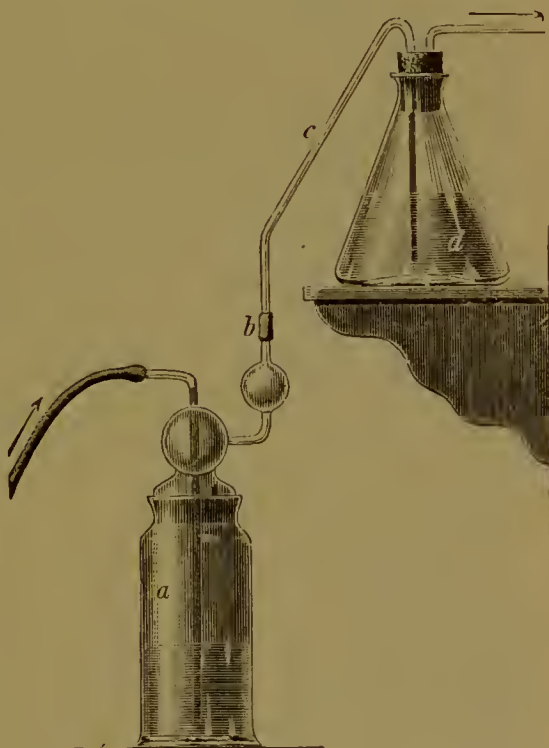


FIG. 2.

<sup>1</sup> *Z. anal. Chem.*, 1883, 22, 520.

The rubber surfaces exposed to bromine should be as small as possible. When the precipitated peroxide is seen to have separated out clearly, the current of air is stopped; fifteen to twenty minutes' treatment suffices for even such considerable amounts of manganese as occur in pyrolusite or ferro-manganese. The liquid must remain distinctly ammoniacal from start to finish for the precipitation to be complete and the formation of nitrogen bromide avoided. After the precipitation, the flask  $\alpha$  is replaced by one containing ammoniacal water, and air is passed through the liquid for fifteen minutes more, when the precipitate settles readily; it is then filtered off, washed with cold water, and ignited to  $\text{Mn}_3\text{O}_4$ .

The precipitate may be contaminated with silica, and also with cobalt, nickel, zinc, and alkaline earths, if present. In order to check the presence of the latter impurities, the peroxide, before being ignited, is dissolved in hydrochloric acid together with a little sulphurous acid, freed from sulphur dioxide by boiling, and neutralised with ammonia. Ammonium acetate and a little acetic acid are then added, sulphuretted hydrogen passed in, to saturation, and the liquid heated, in a closed pressure-flask for one to one and a half hours, to  $80^\circ$  or  $90^\circ$ . Cobalt, nickel, and zinc are thus precipitated; the filtrate is boiled, rendered strongly ammoniacal, and again treated with bromine. The silica in the precipitate is determined (after ignition to  $\text{Mn}_3\text{O}_4$ ), by evaporation with hydrochloric acid, dissolving out the manganese chloride, and filtering. The presence of chromium in no way affects the determination of manganese by this method.

2. *Manganese Sulphide Method.* This method is seldom adopted, but it has the advantage of yielding a precipitate free from silica and alkaline earths. The manganese acetate solution is first treated with sulphuretted hydrogen to precipitate cobalt, nickel, and zinc, and the filtrate is made strongly ammoniacal. Yellow ammonium sulphide is added to the boiling solution, the boiling continued for a few minutes, and the precipitate allowed to settle; it should consist of green anhydrous manganese sulphide, and is at once filtered off and washed with water containing ammonium sulphide. The filtrate is apt to retain inconsiderable amounts of manganese. The filter and precipitate are burnt wet, roasted to  $\text{Mn}_3\text{O}_4$ , and finally ignited strongly for half an hour.

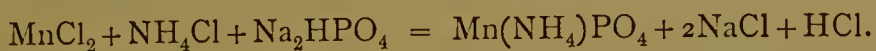
In a complete analysis of an iron or manganese ore, the filtrate from the manganese sulphide can be used for the determination of the alkaline earths.

3. *Manganese Ammonium Phosphate Method.* This method, devised by Gibbs,<sup>1</sup> has been improved by Böttger.<sup>2</sup> A quantity of ammonium

<sup>1</sup> *Z. anal. Chem.*, 1868, 7, 101; *Chem. News*, 1868, 17, 195.

<sup>2</sup> *Ber.*, 1900, 33, 1019; *Chem. News*, 1900, 82, 247.

chloride, corresponding to five to ten times the quantity, in molecular proportion, of the manganese present, is added to the neutralised solution of the manganese. The liquid is heated to boiling in a porcelain or platinum dish, and a considerable excess of di-sodium phosphate, in 12 per cent. solution, added. The precipitation takes place in accordance with the equation:—



To ensure complete precipitation, the liberated acid is neutralised with ammonia and the liquid heated until the precipitate changes from the amorphous form to glittering pink crystals. These are filtered off, thoroughly washed with hot water, and ignited over the blast to manganese pyrophosphate.

Of the foregoing gravimetric methods, the precipitation of iron and alumina as basic acetates by the addition of alkaline acetates after neutralisation of the oxidised chloride solution, is to be recommended as the most practical. The manganese can then be separated from the cold filtrate in a more or less pure condition by the direct addition of about 50 c.c. of bromine water, which is well stirred into the solution. After an interval of about one minute, 20 to 25 c.c. of ammonia (1 : 1) are added, the solution again stirred vigorously, and then boiled for some minutes. The precipitate is allowed to settle, the clear supernatant liquid decanted off, the precipitate collected, dissolved in a little hydrochloric acid, traces of copper removed by sulphuretted hydrogen, any iron or alumina separated, after oxidation of the filtrate from the copper, as basic acetates, one or two drops of acetic acid added, and sulphuretted hydrogen passed through the boiling solution to precipitate any traces of nickel. The clear filtrate is boiled to remove sulphuretted hydrogen, oxidised with bromine, the manganese precipitated pure with ammonia, as above, filtered off, ignited, and weighed as  $\text{Mn}_3\text{O}_4$  (Lambert).

**Chromium.**—Whereas ordinary chromiferous iron ores dissolve without difficulty in hydrochloric acid, chromite (chrome iron ore) has to be rendered soluble by fusion. Half a gram of the latter, previously ground fine and sieved through linen, is mixed in a silver dish with 5 to 6 g. of sodium hydroxide, with a superimposed layer of 3 to 4 g. of sodium peroxide and heated very gradually with a luminous flame.<sup>1</sup> After five minutes, the edges of the sodium hydroxide should begin to melt, and after ten minutes the whole mass; the fusion is then continued for an hour, the melt allowed to cool and extracted with water. Silver is not proof to the action of sodium peroxide, and therefore nickel crucibles are frequently used, or, when contamination with nickel is to

<sup>1</sup> Spiller and Kalman, *Chem. Zeit.*, 1893, 17, 880, 1207, 1360; 1897, 21, 3; *J. Iron and Steel Inst.*, 1893, ii., 537.



be avoided, copper crucibles.<sup>1</sup> The solution of the melt is yellow or green, according to the amount of manganese present; in the latter case small quantities of sodium peroxide (0.3 to 0.6 g.) are added very gradually until the sodium manganate colour disappears and the solution becomes the clear yellow colour of sodium chromate. To remove the excess of peroxide, carbon dioxide is passed into the solution for an hour and the liquid allowed to stand in a warm place for fifteen minutes. The entire residue should be flocculent, if the fusion was complete.

McIvor and Dittmar<sup>2</sup> melt equal parts of borax and fusion mixture together, add 4 g. of this mixture to 0.5 g. of the finely powdered ore, and fuse; after cooling, 2 to 5 g. of fusion mixture are added and the mass fused again. The melt is transferred to a platinum dish, extracted with hot water, filtered, and the residue washed with hot water; the filtrate is acidified with acetic acid, precipitated with lead acetate, and the chromium weighed as  $\text{PbCrO}_4$ .

In the case of ores soluble in hydrochloric acid, 2.0 g. are taken for analysis. The solution is deprived of the bulk of its ferric chloride by the ether method (p. 9) (according to Carnot,<sup>3</sup> this may be omitted), diluted, heated to  $100^\circ$ , treated with a few cubic centimetres of hydrogen peroxide and an excess of ammonia, and boiled; chromium thus remains in solution as ammonium chromate, whilst other heavy metals are precipitated. The precipitate is redissolved and the operation repeated. The combined filtrates are acidified and reduced with hydrogen peroxide, sulphuretted hydrogen being passed in to destroy excess of the latter. Chromium hydroxide is then precipitated by boiling with ammonia, filtered off, washed, ignited, and weighed as  $\text{Cr}_2\text{O}_3$ .

An alternative method, and one particularly adapted to the determination of chromic oxide in chromite, consists in heating for one hour an intimate admixture of the finely ground mineral (0.2 g.) with 4 g. of anhydrous sodium hydroxide and 1.7 g. of magnesia. The mixture is preferably made in a warm dry mortar and subsequently transferred to the crucible. The cooled mass is extracted with a small quantity of boiling water, and the solution boiled to decompose the sodium manganate and ferrate which may be present. The liquid is then filtered, the residue washed, and the filtrate, which should be yellow and quite clear, made up to 100 c.c. Fifty c.c. of the solution ( $=0.1$  g.) are then acidified with a slight excess of dilute sulphuric acid, heated nearly to boiling, allowed to cool, and transferred to a flask containing an excess of ferrous sulphate of known strength. The remaining unoxidised ferrous salt is then titrated with standardised potassium permanganate. The chromium in the remaining 50 c.c. of the original solution of the melt may be determined gravimetrically,

<sup>1</sup> Cf. McKenna, *Eng. and Min. J.*, 1898, p. 607.

<sup>2</sup> *Chem. News*, 1900, 82, 97.

<sup>3</sup> *Z. anal. Chem.*, 1890, 29, 336.

after acidifying the solution and reducing with sulphurous acid. The excess of the latter is removed by boiling and the chromium precipitated by the addition of a slight excess of ammonia to the boiling solution. The precipitate, after being thoroughly washed, is ignited and weighed as  $\text{Cr}_2\text{O}_3$ . It may be examined for impurities after fusion with a small quantity of sodium carbonate and a trace of sodium nitrate and extracting with water (Lambert).

**Zinc.**—Zinc occurs not only in pyrites cinders, but also in various brown hæmatites (especially those which have been formed by the oxidation of pyrites) and in products of magnetic separation. If present in iron ore, it is apt to give trouble in the smelting, owing to the formation of furnace calamine. Even very small quantities are injurious, and their determination is a matter of some difficulty.

According to the commonly adopted method, iron is removed as basic acetate or sulphate and the zinc precipitated from the hot filtrate by passing in sulphuretted hydrogen in presence of acetic acid. Cobalt and nickel are supposed to remain in solution under these conditions, but this is only approximately true, and in order to obtain pure zinc sulphide it is necessary to resort to repeated reprecipitations.

The method is greatly improved when, as suggested by Hampe, formic acid is substituted for acetic acid. The following method for zinciferous iron ores, which often contain lead as well, has been worked out by Kinder.<sup>1</sup> Five grams of the ore are macerated with water and dissolved in hydrochloric acid in a capacious, covered porcelain dish, 20 to 25 c.c. of sulphuric acid (1 : 2 by volume) added, and the whole evaporated until fumes of sulphuric anhydride are evolved. The residue, after cooling, is taken up with water, filtered, the filtrate diluted to 300 to 400 c.c., and saturated with sulphuretted hydrogen. Copper sulphide, if formed, is filtered off, and 25 c.c. of ammonium formate solution and 15 c.c. of formic acid added; if the correct proportion of sulphuric acid has been used, the zinc sulphide should then separate as a flocculent, almost white, precipitate; but in case an excess has been employed, it is safer to neutralise the greater part of the free sulphuric acid with ammonia before adding the ammonium formate. Should the amount of zinc present be considerable, more sulphuretted hydrogen is passed into the warmed liquid. If the zinc sulphide comes down discoloured, it is dissolved in hydrochloric acid, the solution made alkaline with ammonia, then acidified, an excess of 15 c.c. of formic acid added, and reprecipitated by sulphuretted hydrogen as above.

Zinc sulphide may be weighed as such, after having been ignited in a boat or in a Rose's crucible in a current of sulphuretted hydrogen. Or the sulphide may be dissolved in hydrochloric acid and precipitated in the cold with sodium carbonate. The precipitate is gelatinous, but

<sup>1</sup> *Stahl u. Eisen*, 1896, 16, 675.



filters well; after washing four times by decantation and fifteen times on the filter it is free from salts, and may then be ignited and weighed as ZnO.

**Nickel and Cobalt.**—These metals are precipitated together by ammonium sulphide in the filtrates from the iron, aluminium, and zinc; manganese, if present, will be precipitated with them. On treating the precipitate with dilute hydrochloric acid (1:6), the manganese sulphide is dissolved. The residual sulphides of cobalt and nickel are filtered off, washed, and ignited to oxides, or else dissolved, and the contained metals determined electrolytically. The oxides must always be tested for iron and manganese. Cobalt and nickel need not usually be separated, since cobalt rarely occurs in iron ores to any appreciable extent. Should a separation be required, it is best carried out either by the dimethylglyoxime method (p. 66) or by the potassium nitrite method. The determination of nickel is more fully dealt with in connection with the analysis of iron and steel (*cf.* p. 65).

**Calcium and Magnesium.**—These remain in the filtrates from the treatment with ammonium sulphide, and are precipitated, if required to be determined, as calcium oxalate and magnesium ammonium phosphate respectively, in the usual way (*cf.* Vol. I., pp. 405-7).

**Barium.**—Barium may be present in iron ores as heavy spar, in blast furnace slags as barium sulphide, and in certain manganese ores (psilomelane) as an isomorphous constituent. In the first two cases it remains with the undissolved siliceous residue, and is extracted by fusion with alkali carbonate. In the latter case it remains in solution until the calcium has been separated, and is then precipitated by sulphuric acid.

**Alkalis.**—These may have to be determined in charcoal ashes, or in slags from blast furnaces using charcoal. The usual method of decomposing with hydrofluoric acid, separating all other metals by means of ammonium salts, weighing as mixed sulphates, and separating the potassium as platinichloride, may be adopted (*cf.* Vol. I., pp. 520 and 529).

**Copper, Lead, Arsenic, Antimony.**—These impurities can be determined in one and the same sample. Ten grams of the ore are dissolved in hydrochloric acid, with repeated addition of a little nitric acid, the solution filtered and either evaporated or the bulk of the iron removed by the ether-extraction method. The residue is fused with sodium carbonate and the extract added to the main solution. The iron is then reduced to the ferrous state, and sulphuretted hydrogen passed in. The precipitate is washed with dilute sulphuretted hydrogen solution and digested with sodium sulphide. Antimony and arsenic sulphides are precipitated from the filtrate by hydrochloric acid, filtered off, and

warmed with hydrochloric acid and potassium chlorate; tartaric acid, magnesia mixture, and ammonia are then added to the filtered solution. On standing for twenty-four hours, the arsenic is precipitated as magnesium ammonium arsenate, which is ignited and weighed as  $\text{Mg}_2\text{As}_2\text{O}_7$ . The filtrate is acidified and treated with sulphuretted hydrogen, the precipitated antimony sulphide ignited with repeated additions of nitric acid and weighed as  $\text{Sb}_2\text{O}_4$ ; this contains 78.97 per cent. Sb.

The black sulphides insoluble in sodium sulphide are dissolved in nitric acid, evaporated down with a little sulphuric acid, and treated with alcohol. Lead sulphate is thus precipitated and weighed as such. From the filtrate, copper sulphide may be precipitated and ignited to the oxide, or else the copper may be separated electrolytically. In the absence of the usual electrolytic apparatus, the following simple device, described by Ullgren,<sup>1</sup> may be employed. The requisites consist of a small platinum dish, a glass tube 100 mm. long and 30 to 40 mm. wide, tied over at one end with a piece of bladder, and a long strip of zinc 25 mm. wide. The zinc is so bent that one end lies under the platinum dish, whilst the other dips into the glass tube, which is filled with saturated brine and is clamped within 6 to 8 mm. of the dish. On pouring the copper solution into the dish, electrolytic deposition sets in and is completed in from one to two hours. The dish is then washed out with water without breaking the circuit, rinsed with alcohol, warmed for five minutes in an air-bath, and weighed.

When arsenic is determined separately, copper, lead, and antimony may be determined as follows:—The bulk of the iron is removed from the original solution of ore after concentrating somewhat, by means of ether (*cf.* p. 9). The insoluble residue is decomposed by fusion, as above, the filtered extract added to the acid solution, and the whole evaporated to dryness, when the arsenic is expelled as the trichloride. On taking up with dilute hydrochloric acid and passing in sulphuretted hydrogen, the sulphides of copper, lead, and antimony are precipitated; the subsequent operations are carried out as described.

The determination of arsenic alone is conveniently carried out by Ledebur's method. Ten grams of the ore are digested, with frequent agitation, with 120 c.c. of cold hydrochloric acid of sp. gr. 1.19; when dissolved as far as possible, 2 to 4 c.c. of bromine are added, and the liquid warmed up gradually until nearly all the bromine has volatilised. The clear liquid is then poured off, the residue filtered off and washed, and the whole of the solution thus obtained placed in the flask *a* (Fig. 3), together with a solution of 15 g. of arsenic-free ferrous chloride in 60 c.c. of hydrochloric acid of sp. gr. 1.124; the solution is then cautiously distilled over a rose-burner. When about 40 c.c. remain, 50 c.c. of

<sup>1</sup> *Z. anal. Chem.*, 1868, 7, 442.

hydrochloric acid are added and the distillation continued down to a residual volume of 40 c.c. The distillate, which contains all the arsenic,

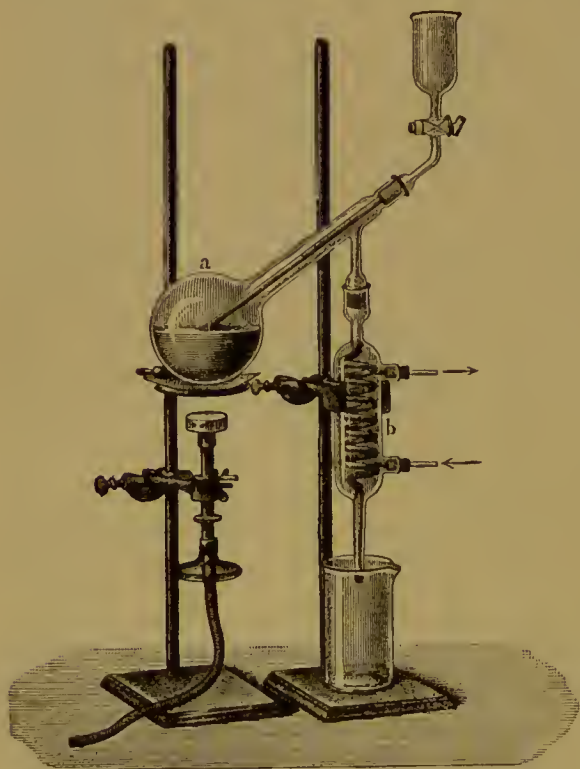


FIG. 3.

is treated with sulphuretted hydrogen at about  $70^{\circ}$ . After standing for several hours, the arsenic sulphide is filtered off, washed till the filtrate is neutral, dissolved in ammonium carbonate, reprecipitated by means of hydrochloric acid and sulphuretted hydrogen water, the precipitate collected on a tared filter paper, and washed till free from chlorine. The filter is then dried, allowed to cool in a desiccator, and the arsenic weighed as trisulphide; this contains 60.93 per cent. of arsenic.

A less fragile form of distilling flask has been described by Kleine.<sup>1</sup>

**Phosphoric Acid.**—The only method now in use for determining phosphoric acid is by precipitation as ammonium phosphomolybdate,  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ . When properly carried out, it is one of the most accurate determinations known. In order to secure correct results, however, it is necessary to take into account the conditions under which quantitative precipitation takes place. The various points to be considered have been summarised and the results of Fresenius and others confirmed by Hundeshagen;<sup>2</sup> his main conclusions are as follows:—

(1) Free hydrochloric or sulphuric acids, free nitric acid (over 80 molecules to 1 molecule of phosphoric acid), and salts of polybasic acids (especially sulphuric and boric acids) prevent complete precipitation.

(2) Free nitric acid (26 to 80 molecules per molecule of phosphoric acid) retards precipitation.

(3) Free nitric acid (less than 26 molecules) and salts of monobasic acids (chlorides, bromides, etc.) have no harmful action.

(4) Ammonium nitrate greatly accelerates precipitation, so much so that 0.5 g. brings down all the phosphorus, unless present in mere traces, in a few minutes.

(5) High temperatures favour precipitation. With only 0.05 g. of

<sup>1</sup> *Stahl u. Eisen*, 1904, 24, 248.

<sup>2</sup> *Z. anal. Chem.*, 1889, 28, 141; *Chem. News*, 1889, 60, 169, 177.



phosphoric acid in 100 c.c., the precipitate is instantly formed at boiling temperature, especially on rubbing with a glass rod. Precipitates from hot solutions are crystalline and filter better than those from cold solutions.

(6) There must be at least twice as much molybdic acid as is theoretically required—that is, at least 24 molecules to 1 of phosphoric acid.

(7) Cold water, very dilute acids, and solutions of ammonium salts have a slight solvent action on the precipitate.

It is important that the liquid to be precipitated should be free from silicic acid, since this yields a compound with molybdic acid closely resembling the phospho-molybdate. Also, the phosphorus must be present wholly as phosphoric acid, since the lower oxides of phosphorus are not completely precipitated. After drying at  $130^{\circ}$  to  $150^{\circ}$ , the precipitate consists of  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ , and contains 3.782 per cent.  $\text{P}_2\text{O}_5$ , or 1.651 per cent. of phosphorus.

Limonite must be ignited before solution to remove the organic matter which is always present, as this interferes with the complete precipitation of the phosphoric acid.

The determination of phosphorus is carried out as follows:—From 0.5 to 10 g. of the sample are weighed out according to the approximate proportion of phosphorus present; for basic slag 0.5 g.; for calcareous ironstone, limonite, pea iron ore, and puddle slag 1 g.; for red and brown hæmatites and magnetic ores 5 g.; and for ores for Bessemer pig 10 g. The ore is dissolved in concentrated hydrochloric acid, the solution evaporated to dryness, taken up with hydrochloric acid and evaporated down again, and the residue digested with 10 to 20 c.c. of nitric acid of sp. gr. 1.2. After diluting, warming, and filtering, and washing the residue with water containing nitric acid, the volume of the liquid should not exceed 20 c.c. if 1 g. of the sample was taken, or 50 c.c. for larger quantities. The solution is then neutralised with ammonia, 1 g. of ammonium nitrate added, the liquid heated to boiling, and precipitated with 25 to 50 c.c. of molybdic acid solution (prepared as described on p. 2). The precipitation may be regarded as complete after standing for half an hour at  $70^{\circ}$  to  $80^{\circ}$ . The phospho-molybdate is then filtered off and washed till free from iron with water containing 5 per cent. by volume of concentrated nitric acid. As the precipitate is apt to retain traces of iron, v. Reis<sup>1</sup> recommends decanting off the supernatant liquid, washing the precipitate on to the filter, and paying special attention to the washing of the edges of the latter. The precipitate is further purified by means of 15 c.c. of citrate solution (10 g. of citric acid and 100 c.c. of ammonia of sp. gr. 0.91 made up to a litre), which is added gradually from a pipette, and is then dissolved in warm dilute

<sup>1</sup> *Stahl u. Eisen*, 1888, 8, 827.

ammonia; the solution is collected in the vessel in which the original precipitation was effected, and the filter paper washed with a 2.5 per cent. solution of ammonia. Hydrochloric acid is added to the solution thus obtained to just short of reprecipitation, then 2 c.c. of magnesia mixture and one-third of the whole volume of ammonia; the liquid is well stirred and allowed to stand for fifteen minutes. Very small amounts of phosphate may need longer standing; in any case, the precipitate should settle clearly out of the liquid. The magnesium precipitate is filtered off, washed with dilute ammonia, burnt wet in a platinum crucible, ignited till perfectly white, and weighed as  $\text{Mg}_2\text{P}_2\text{O}_7$ . If it is not quite white, a few drops of nitric acid may be added, evaporated off, and the ignition repeated.

In the case of an arsenical ore, certain precautions are necessary, since both the molybdate and the magnesium precipitates will contain arsenic. If there is but little arsenic, advantage may be taken of the fact that magnesium ammonium arsenate requires much more time to separate out—at least twelve hours—than the phosphate. When an appreciable proportion of arsenic is certainly present, the magnesium precipitate is dissolved in hydrochloric acid, sulphuretted hydrogen passed in at  $70^\circ$ , the arsenic sulphide filtered off, the filtrate boiled down with a little potassium chlorate and reprecipitated with magnesia mixture.

Titanium, if present, also gives a precipitate with molybdic acid. In this case the ore is fused with four times its weight of fusion mixture and the melt extracted with water, when titanium dioxide remains undissolved. The filtrate is freed from silica by evaporation with hydrochloric acid, and is then treated as above.

As an alternative to conversion into magnesium ammonium phosphate, the molybdate precipitate may, as proposed by Finkener, be weighed directly. For this purpose the ammoniacal solution is evaporated till nearly free from ammonia, an adequate quantity of dilute nitric acid added, and the evaporation continued. When the mass becomes pasty, it is cautiously taken to dryness over an asbestos sheet or wire gauze, and heated to  $130^\circ$  to  $150^\circ$  until a watch-glass laid on the dish shows no sublimate after half a minute. The residue is then allowed to cool in a desiccator and weighed.

Ores containing heavy spar must invariably be treated by fusion or by solution in acid and subsequent fusion of the residue, since the latter, according to v. Jüptner, sometimes retains more than half of the total phosphorus.

The following is a brief description of the method of determining the phosphorus in iron ores in use at the laboratory of the Monongahela Furnace McKeesport, P.A.<sup>1</sup>

From 2 to 5 g. of the ore are digested with 75 to 150 c.c. of concentrated

<sup>1</sup> *Methods of Iron Analysis*, p. 12 (see Literature, p. 89).



hydrochloric acid and the solution evaporated to hard dryness. About 100 c.c. of strong hydrochloric acid are poured on the residue and the mixture boiled until the solution is concentrated to about half this volume; water is then added and the diluted solution filtered, keeping the volume of the filtrate as small as is convenient. The solution is then evaporated with nitric acid until the hydrochloric acid is driven off. The insoluble residue is ignited and the silica driven off with hydrofluoric acid. The residue is fused with sodium carbonate, dissolved in nitric acid, and the solution filtered into the main solution. The whole is then placed in a 500 c.c. Erlenmeyer flask and dilute ammonia added until the solution becomes pasty and smells ammoniacal; the precipitate is then dissolved in a slight excess of nitric acid, and the solution heated up to  $80^{\circ}$ , when 40 c.c. of the molybdate solution are added. The solution is agitated by a current of air for about five minutes, filtered, while still warm, on a tared filter paper, and after washing thoroughly with distilled water the yellow precipitate of phosphomolybdate of ammonia is dried and weighed; or, it can be dissolved in ammonia and the contained phosphorus estimated.

**Sulphur (Sulphides) and Sulphuric Acid (Sulphates).**—These are determined together. In presence of an excess of ferric chloride in solution, small precipitates of barium sulphate separate with difficulty and often contain iron (*cf.* Vol. I., pp. 273-5). It is therefore preferable to decompose the ore by fusion rather than to dissolve it in acid. Three grams of ore are mixed with an equal quantity of sodium carbonate containing 10 per cent. of potassium nitrate, gradually heated to a red heat in a platinum crucible, and fused for some time. The melt is extracted with hot water, the filtrate evaporated to dryness with hydrochloric acid, the residue taken up with hydrochloric acid and hot water, the silica filtered off, the clear acidified solution precipitated with barium chloride, and the total sulphur weighed as barium sulphate in the usual way.

**Titanium.**—The determination of titanium, which frequently occurs in Swedish and Norwegian magnetic ores, is somewhat complicated, but has been facilitated by the introduction of the ether-separation process. The following method, described by Ledebur, is employed to a considerable extent:—

Five grams of the ore are dissolved in hydrochloric acid, when part of the titanium is left behind in the residue. The solution is extracted with ether to remove the iron, as described on p. 9. Phosphoric and titanous acids remain in the aqueous solution, though the latter may separate out in flocculent particles. Meanwhile the residue is melted with fusion mixture, the silica separated in the usual way, ignited, and evaporated with hydrofluoric acid, any residue of titanium dioxide being again treated with fusion mixture. The original solution

and the extracts of the two melts are then united, neutralised, and boiled with sodium acetate, whereby any residual iron, together with alumina, phosphoric acid, and titanitic acid, are separated from the chlorides of the other metals present. The basic acetate precipitate, after washing with hot water, is again fused with fusion mixture and lixiviated; the residue then contains ferric oxide, alumina, and all the titanitic acid. It is washed, dried, and again fused with not less than twelve times its weight of acid potassium sulphate, until every particle is dissolved. The melt is dissolved in cold water, treated with sulphuretted hydrogen, filtered from any precipitate of copper or platinum sulphide, and boiled in a conical flask for an hour. The titanium dioxide is thus precipitated and is filtered off, washed, dried, ignited, and weighed.

Ledebur has more recently (1908) proposed to separate the bulk of the iron from titanium by reducing the ore in a current of hydrogen and dissolving the metallic iron formed in sulphuric acid (1:40); the silica in the residue is then removed by treatment with hydrofluoric acid. Trulot and Riley<sup>1</sup> have, however, shown that it is necessary to evaporate with sulphuric acid, and ignite, as otherwise titanium is volatilised as the fluoride  $\text{TiF}_4 \cdot 2\text{HF}$ . The titanitic acid is then dissolved by fusion with acid potassium sulphate, the melt dissolved in water, and the titanitic acid precipitated by prolonged boiling. Any ferric iron present is reduced to the ferrous condition by passing sulphuretted hydrogen into the solution, whereby any precipitation of basic sulphate is prevented. Should the ore contain more than 0.1 per cent. of phosphoric acid, the residue, after treatment with hydrofluoric acid, is fused with sodium carbonate, or otherwise the phosphoric acid would be precipitated with the titanium. The aqueous solution then contains the whole of the phosphoric acid, whilst the titanitic acid remains in the residue and is fused with acid potassium sulphate.

**Tungsten.**—Iron ores proper scarcely ever contain tungsten, but it may occasionally be necessary to determine this metal in wolframites. The first step is to bring the mineral into a soluble form; this can be readily effected, according to Hempel,<sup>2</sup> by fusing one part of the finely-powdered sample with four parts of sodium peroxide in a silver crucible, when a melt soluble in water is obtained in a very few minutes. The filtered extract is boiled with an excess of nitric acid, and the precipitated tungstic acid filtered off, washed, ignited, and weighed; it is then evaporated with hydrofluoric acid, ignited, and weighed again; the difference represents the contained silica. Should tin be present, the mixture of acid oxides is fused with potassium cyanide, the aqueous extract filtered from reduced tin, and the tungstic acid precipitated as before.

<sup>1</sup> *Stahl u. Eisen*, 1906, 26, 88.

<sup>2</sup> *Z. anorg. Chem.*, 1893, 3, 193.

When arsenic and phosphorus are present, Bullnheimer<sup>1</sup> adopts the following method:—About 3 g. of sodium hydroxide are added in the sodium peroxide fusion, and any permanganate which may be present in the extract reduced with hydrogen peroxide. One half of the filtrate from the extract is treated with 20 g. of ammonium nitrate, the silica and stannic acid allowed to settle out, and then magnesia mixture added. If the settling is omitted, some tungsten will come down with the magnesium precipitate. The filtrate is then rendered faintly acid with nitric acid and 20 to 30 c.c. of mercurous nitrate solution (200 g. mercurous nitrate and 20 c.c. of concentrated nitric acid made up to a litre) added. After standing for a few hours, ammonia is added nearly to neutrality; an excess of mercuric oxide suspended in water is preferred by some for the neutralisation (Lambert). The precipitate is then allowed to settle, filtered off, washed with water containing mercurous nitrate, ignited, and weighed. The mercurous nitrate should, of course, leave no residue upon a blank ignition of a sample of the solid salt.

**Carbonic Acid.**—If required, this may be estimated by the loss of weight on treatment with acid in a Schrötter's or similar apparatus. For a more accurate method, see Vol. I., p. 148.

**Fluxes** are analysed by the same methods as ores. In determining calcium and magnesium, which are present in considerable quantity in fluxes, it is advisable to weigh out quite small quantities of the finely ground and intimately mixed sample; for the other constituents, of which the percentage, as a rule, is low, 1 to 3 g. should be taken.

**Slags.**—The analysis of slags does not necessitate any exceptional treatment. Highly ferruginous refinery slags behave like difficultly soluble ores. Basic slags owe their value to a high content of phosphorus, and are often assayed for this constituent alone, the method given on p. 23 being carried out on small quantities of material; when many analysis are required, a centrifuge will be found useful. The determination of citrate-soluble phosphorus is described in the section on "Artificial Manures," p. 400.

Full analyses of blast furnace slag are frequently required, and are carried out like any other silicate analysis, except that alkaline fusion is unnecessary. The slag contains a certain amount of sulphur as barium, calcium, and manganese sulphides, and this is determined by the sulphuretted hydrogen method as applied to cast iron (p. 80).

The shortened method of analysis of blast furnace slag, described by Textor,<sup>2</sup> is not quite accurate, but suffices for most purposes. Three samples of the slag are weighed out: No. 1, of 1.325 g., for the determination of calcium and magnesium; No. 2, of 0.5 g., for silica and alumina; and No. 3, also of 0.5 g., for sulphur. Nos. 1 and 2 are

<sup>1</sup> *Chem. Zeit.*, 1900, 24, 870; *J. Iron and Steel Inst.*, 1901, i., 529.

<sup>2</sup> *J. anal. and applied Chem.*, 1893, 7, 25.



each stirred up with 25 c.c. of boiling water, together with 25 c.c. and 10 c.c. respectively of hydrochloric acid (1 : 1), and boiled, with continual agitation, until dissolved. No. 2 is oxidised with a little nitric acid, evaporated to dryness, and heated to drive off hydrochloric acid. No. 1 is similarly oxidised, diluted to 300 or 350 c.c., treated with 25 c.c. of strong ammonia (which is added very gradually, to avoid precipitation of magnesia), and made up to 530 c.c. Two hundred and fifty c.c. of the filtrate, corresponding to 0.625 g. of slag, are taken for the determination of magnesium, and 200 c.c., corresponding to 0.5 g., for that of calcium. Both portions are boiled with 25 c.c. of ammonium oxalate solution; the portion for the magnesium estimation is then cooled and made up to 300 c.c., whilst that for the determination of the calcium is filtered, the precipitate washed, dissolved in sulphuric acid, and titrated with potassium permanganate. Of the diluted magnesium portion, 240 c.c., corresponding to 0.5 g. of slag, are filtered off, and poured into 10 c.c. of sodium phosphate solution and 10 c.c. of strong ammonia contained in a beaker; precipitation is aided by blowing air through the liquid for ten minutes.

Meanwhile all the silica in sample No. 2 will have been rendered insoluble. The residue is digested with 15 c.c. of concentrated hydrochloric acid. During this time the ammonium magnesium phosphate, precipitated as above, is filtered off, washed, ignited, and weighed with the usual precautions. The residue from No. 2 is then taken up with hot water, boiled, and filtered, and the silica washed, ignited, and weighed. Alumina is precipitated in the filtrate with ammonia. Iron is usually a very minor constituent, and is included with the aluminium; if it be present in considerable quantity, a separate sample of the slag is assayed for iron volumetrically. Manganese, if present, will, for the most part, go into the magnesium precipitate; the method is not applicable to the more manganiferous kinds of slag. Finally, sulphur is determined in sample No. 3, by suspending it in 150 c.c. of hot water, adding starch solution and 15 c.c. of standard iodine solution (1 c.c. = 0.1 per cent. of sulphur), then 30 c.c. of concentrated hydrochloric acid, and titrating back the excess of iodine.

## 2. VOLUMETRIC ANALYSIS.

**Iron.**—The volumetric determination of iron is based on a process either of reduction or of oxidation by means of a standard solution. Iron ores never yield a wholly ferrous or wholly ferric solution in the ordinary way, so that titration has to be preceded either by complete oxidation or reduction as the case may be. The most important methods are:—Oxidation, either with potassium permanganate or bichromate, and reduction with stannous chloride.



1. *Permanganate Method.* The decolorisation of potassium permanganate by ferrous salts is a very sharp and delicate reaction; it takes place according to the following equation:—



Iron, in the ferrous condition, can thus be determined by adding permanganate, until a faint pink colour becomes permanent. One c.c. of an exactly decinormal solution of potassium permanganate would correspond to 5.585 mg. of iron; in practice, a solution containing about 5 g. per litre is made up. Permanganate solutions were formerly regarded as unstable, but it is now known that if they are boiled when made up, and then protected from light, they remain unchanged for months (*cf.* Vol. I., p. 101).

The standardisation should take place under the same conditions as the actual application. For this purpose iron wire was formerly employed, which was assumed to contain 99.7 to 99.8 per cent. of iron, but its use is now entirely discredited; electrolytic iron, as recommended by Classen, Treadwell, and others, is inconvenient to prepare, and has also been proved to be unreliable in regard to its purity (*cf.* Vol. I., pp. 106-8). The most trustworthy substance as a basis for the standardisation appears to be sodium oxalate, originally proposed by Sørensen<sup>1</sup> (*cf.* Vol. I., p. 105). This salt is not hygroscopic, and is manufactured in a chemically pure form by Kahlbaum. A weighed quantity of it (after drying in the steam-bath, if extreme accuracy be desired) is dissolved in water, acidified with sulphuric acid, heated to 70°, and titrated with the permanganate solution. 0.10 g. of sodium oxalate corresponds to 14.93 c.c. of an exactly decinormal solution of permanganate. Iron wire can also be used as a basis for the standardisation of permanganate, provided its content of iron has been previously determined by means of a permanganate solution standardised by sodium oxalate; the details of this method are fully described in Vol. I., pp. 105-8.

The determination of iron by means of permanganate is best carried out in solutions containing no acid other than sulphuric. Wherever possible, therefore, ores for assay should be dissolved in sulphuric acid; if this be not feasible, the sample is dissolved in hydrochloric acid and the solution evaporated with sulphuric acid. Carbonaceous ores, bog ores, etc., must be previously freed from organic matter by roasting. A solution of 0.5 to 1.0 g. of ore is prepared and the iron reduced to the ferrous condition by means of a piece of zinc (free from iron and carbon) wrapped round with platinum; reduction is complete when no coloration is produced by potassium thiocyanate. The solution is then made up to 100 c.c. with boiled water, and portions of 20 c.c. titrated.

<sup>1</sup> *Z. anal. Chem.*, 1897, 36, 639; 1903, 42, 333; 1905, 44, 156.

Zinc dust, which has the advantage of acting almost instantaneously, is sometimes recommended as a reducing agent. In this case the solution must not approach neutrality, for then iron hydroxides may be precipitated; on the other hand, any large excess of acid tends to retard the action of the zinc. It is always necessary to make a blank determination of iron in the zinc dust.

According to Carnegie,<sup>1</sup> the reduction is advantageously effected by covering the bottom of a narrow beaker with zinc dust, previously passed through a muslin bag, and a measured volume of the iron solution, nearly neutralised with ammonia, added; after vigorous stirring, a known volume of dilute sulphuric acid is introduced and the liquid again well stirred. An aliquot part of the clear solution is then withdrawn by means of a pipette provided with a filtering extension over the nozzle. C. Jones<sup>2</sup> recommends preferably the use of a reducing tube consisting of a glass tube tied over at the bottom with muslin and charged with zinc dust which has passed a 40 to 60 mm. mesh sieve. An iron solution is fully reduced after being poured through once or oftener, and is then ready for titration; a specially designed tube may be employed, which holds 300 g. of zinc and serves for sixty reductions.<sup>3</sup>

It is, in general, advantageous to circumvent the tedious preparation of a purely sulphuric solution of iron ore. Hydrochloric acid solutions do not always lend themselves to titration with permanganate, since the acid may react with production of free chlorine according to the equation:—



With a small excess of free acid, a very dilute solution, and low temperature, the titration may, however, be carried out without danger from this secondary reaction; in any case, the formation of chlorine is easily detected by the smell. The danger is entirely obviated when a large excess of manganous salt is present. A point greatly in favour of hydrochloric solutions is, that they can be reduced with stannous chloride instead of with zinc.

This method, as worked out by Kessler<sup>4</sup> and improved by Reinhardt,<sup>5</sup> is as follows:—The solution of iron ore in hydrochloric acid is decolorised at boiling temperature by stannous chloride, and 60 c.c. of an aqueous solution of mercuric chloride added to remove the excess of the reducing agent; the solution is diluted, and 60 c.c. of an acid solution of manganous sulphate added. The titration with permanganate then

<sup>1</sup> *J. Chem. Soc.*, 1888, 53, 468.

<sup>2</sup> *Chem. News*, 1889, 60, 93.

<sup>3</sup> *Z. anal. Chem.*, 1890, 29, 59; *J. Amer. Chem. Soc.*, 1899, 21, 723.

<sup>4</sup> *J. Iron and Steel Inst.*, 1885, p. 299.

<sup>5</sup> *Stahl u. Eisen*, 1884, 4, 704; 1889, 9, 584; *J. Iron and Steel Inst.*, 1889, i., 400; 1900, i.,

proceeds smoothly and accurately. Since the ferric chloride produced is apt to mask the end-reaction, it is well to add phosphoric acid, which yields colourless ferric phosphate. Reinhardt's solutions are made up in the following concentrations:—Potassium permanganate 6 g., mercuric chloride 50 g., and stannous chloride containing 30 g., of tin, per litre. The manganous sulphate solution is made up with  $66\frac{2}{3}$  g. of manganous sulphate,  $333\frac{1}{3}$  c.c. of phosphoric acid (sp. gr. 1.3) and 133 c.c. of strong sulphuric acid in the litre.

The strength of the permanganate solution should always be fixed by means of ferric oxide or of an iron ore of known iron-content; this is dissolved, reduced, and then titrated, as above.

Experiments made to determine the influence of copper, arsenic, chromium, nickel, titanium, lead, and antimony on the determination of iron by this method have shown that only antimony has an appreciable influence on the results; as this metal only occurs in iron ores to a limited extent, this influence is not regarded as important.<sup>1</sup>

*2. Bichromate Method.* Whereas the volumetric estimation of iron with potassium permanganate necessitates special conditions in presence of hydrochloric acid, and is also affected by the presence of organic matter, which is frequently contained in ores or generated as hydrocarbons from alloys, the volumetric estimation of iron with potassium bichromate is free from these drawbacks. An external indicator is required in the titration, since the end-reaction between the yellow bichromate and the green chromic chloride solutions cannot be observed directly. The oxidation takes place according to the equation:—



To carry out the determination, the ore is dissolved in hydrochloric acid, reduced with zinc or with stannous chloride, the excess of the latter removed with mercuric chloride, the solution diluted somewhat, rendered strongly acid with dilute sulphuric acid, and titrated in aliquot portions with potassium bichromate solution. A drop of the solution is taken out and mixed with a drop of very dilute potassium ferricyanide solution from time to time during the titration; a blue, and then a green, coloration is produced so long as any iron remains unoxidised; after the oxidation is complete, the colour will remain pure yellow. The approximate quantity of bichromate required is first determined by a preliminary titration; one or more further titrations are then made, the test for the completion of the reaction being made by adding the bichromate solution in quantities of 0.1 c.c. at a time.

The standard solution is quite permanent, and is made up by dissolving 4.90 g. of fused potassium bichromate in a litre of water.

<sup>1</sup> Cf. *Stahl u. Eisen*, 1908, 28, 508.



One c.c. of this solution is = 5.585 mg. Fe. The strength of the solution should be checked by means of a standard ferric solution.

3. *Stannous Chloride Method.* Since standardisation by means of iron wire is unreliable, either chemically pure ferric oxide or an oxide of ascertained iron-content is used for fixing the strength of the solution. The former may be prepared according to the method described by Wdowiszewski.<sup>1</sup> A simpler plan, however, is to stock a large quantity of some pure iron ore, and to estimate the contained iron accurately by quantitative determinations. For each standardisation 5 g. of the ore are dissolved, made up to 100 c.c. and 20 c.c. (= 1 g. of ore) titrated. The most suitable material is magnetic ore, as it is not hygroscopic; red hæmatite has a tendency to take up moisture when powdered. Ferric chloride solutions should not be used as the basis for standardisation, since they do not keep without undergoing change.

The ore is dissolved in concentrated hydrochloric acid, carefully oxidised with potassium chlorate, the solution freed from chlorine by boiling, and made up to a definite volume, aliquot parts of which are titrated with the stannous chloride solution. To make up the latter, granulated tin is heated with concentrated hydrochloric acid until the evolution of hydrogen ceases, and the liquid diluted with nine volumes of hydrochloric acid (1 : 2). The strength of this solution can under no circumstances be regarded as constant, but rapid oxidation can be avoided by storing it in a bottle having a tap at the bottom and connected at the upper end with a supply of coal gas or hydrogen. The titration is carried out at boiling temperature, in presence of a considerable excess of hydrochloric acid. The reaction is as follows:—



With practice it is quite easy to titrate from the yellow ferric solution to the colourless ferrous solution without further aids, but the reaction slows down somewhat towards the end, so that time must be allowed for the stannous chloride to react. An alternative and safer method is to add stannous chloride in slight excess, cool, dilute, add starch paste, and titrate back with standard iodine solution. The latter is made up by dissolving about 10 g. of iodine in potassium iodide solution and diluting to 1 litre, and is standardised against the solution of stannous chloride.

For the actual determination, from 2.5 to 5.0 g. of the ore are dissolved as above, the solution made up to 100 c.c., and 20 c.c. (= 0.5 to 1.0 g. of ore) taken for the titration. A preliminary titration is first made, to ascertain about how much stannous chloride is required for the reduction; in the final titration the bulk of the stannous chloride solu-

<sup>1</sup> *Stahl u. Eisen*, 1901, 21, 816; *J. Iron and Steel Inst.*, 1901, ii., 521.



tion is added at once, and the estimation completed by the subsequent addition of small portions at a time.

The titration can also be effected by using sodium molybdate as an external indicator;<sup>1</sup> a minute excess of stannous chloride reduces the molybdate and gives a blue coloration.

4. *Determination of Ferrous and Ferric Iron.* When iron is present in an ore in both stages of oxidation, there is no difficulty in determining firstly the ferrous iron, and secondly the ferric iron, by one or other of the above methods. This can be done either on one and the same portion of the sample, or on separate portions.

The solution must be made up so as to avoid any oxidation through contact with air. For this purpose the method proposed by Jahoda<sup>2</sup> for dissolving standard iron wire may be adopted. The ore is placed, together with a pinch of sodium bicarbonate, in the flask *a* (Fig. 4), acid poured in, and a cork fitted with a glass tube bent twice at right angles inserted. The open end of the latter dips into a beaker, *b*, containing a dilute solution of sodium bicarbonate. When solution is complete and the flask is allowed to cool, some of the bicarbonate sucks back, but is prevented from filling the flask owing to the evolution of carbon dioxide; this is repeated as the cooling proceeds, so that a solution of ore in an atmosphere of pure carbon dioxide is finally obtained. The Contat-Göckel bulb (see Vol. I., p. 106) acts on the same principle and is much more compact.

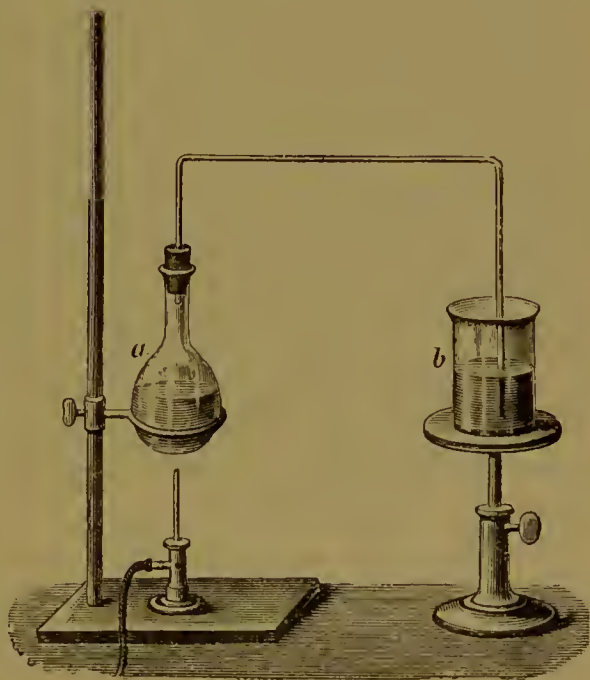
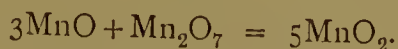


FIG. 4.

**Manganese.**—The most commonly used volumetric methods for manganese are based on the following reaction, which was first applied by Guyard<sup>3</sup>:—



Owing, however, to the acidic nature of manganese dioxide, it has a great tendency to form compounds with manganous oxide, such as  $\text{MnO} \cdot 5\text{MnO}_2$ ; consequently the above reaction never quite holds good,

<sup>1</sup> Cf. Zengelis, *Ber.*, 1901, 34, 2046; *J. Soc. Chem. Ind.*, 1901, 20, 840.

<sup>2</sup> *Z. angew. Chem.*, 1889, 2, 87.

<sup>3</sup> *Chem. News*, 1863, 8, 292.

and the value of a standard solution cannot be deduced from its content of permanganate, but must be ascertained empirically.

According to some methods, the manganese is first separated as dioxide, this redissolved as a manganous salt, and titrated with permanganate. In others, iron is removed and the filtrate titrated directly, either with or without adding an excess and titrating back. The following method is that of Volhard,<sup>1</sup> modified by N. Wolff.<sup>2</sup>

In this method all the manganese must be present as manganous oxide and all the iron as ferric oxide, in hydrochloric acid solution. The iron is precipitated by means of zinc oxide and the manganese titrated, without filtering, at a temperature of 80°, with standard permanganate.

The permanganate solution is made up by dissolving 9 g. in 1000 c.c. Its value is determined by reducing, say, 30 c.c. of the solution itself, by means of hydrochloric acid, to manganous chloride, neutralising with zinc oxide, and titrating at 80°. As the result of numerous investigations, carried out independently and with solutions of different concentrations, it was found that 100 c.c. of the reduced solution require 66 c.c. for titration, as against 66.66 c.c. calculated from the equation given above. When the exact permanganate content of a solution has been determined by means of sodium oxalate, its value for the estimation of manganese is thus ascertained. Whilst this correction is still fairly generally accepted, more recent investigations by De Koninck<sup>3</sup> indicate that the reaction does proceed exactly in accordance with the equation given above; the factor 0.2952 for the conversion of the iron-value of the permanganate solution to the value for manganese is therefore applicable.

To carry out the determination in the case of ores and slags, which leave a manganese-free residue on treatment with hydrochloric acid, 1 g. is weighed out for ores containing up to 20 per cent. of manganese, and 0.5 g. for those containing 20 to 50 per cent. The sample is weighed into a litre conical flask, digested with 20 c.c. of hydrochloric acid (sp. gr. 1.19), and boiled, with the addition of 3 g. of potassium chlorate, until all chlorine is expelled. Ores not answering to this description are evaporated in a covered porcelain dish with hydrochloric acid and a little chlorate until the separated silica has become granular, the residue digested with hydrochloric acid and filtered. The residue from the filtration is then fused with mixed carbonates, and the melt subjected to the same treatment as the original material. The combined filtrates should be evaporated to 100 c.c. if necessary. In all cases three samples should be dissolved, and the solutions finally collected in litre conical flasks.

<sup>1</sup> *Chem. News*, 1879, 40, 207.

<sup>2</sup> *J. Iron and Steel Inst.*, 1885, p. 301; *Stahl u. Eisen*, 1890, 11, 377.

<sup>3</sup> *Bull. Soc. Chim. Belg.*, 1904, 18, 56; *Chem. Centr.*, 1904, I., 1429.

When the substance contains little iron and much phosphorus or arsenic (*e.g.*, basic slags), sufficient iron must be added to ensure the precipitation of all the phosphoric and arsenic acids. The iron is added either in the form of manganese-free oxide or chloride, or else 0.5 g. of iron ore of known manganese content is dissolved with the sample. The solutions are tested for ferrous iron with potassium ferricyanide, and, if necessary, oxidised with hydrogen peroxide; they are then boiled so as to obtain all the manganese in the manganous condition. The iron is precipitated with pure ignited zinc oxide suspended in water, which is added in small portions at a time, with thorough agitation, until all the iron is just precipitated; the end-point is indicated by the sudden coagulation of the ferric hydroxide. At this stage the supernatant liquid will still have a brownish colour, but will, as a rule, clear to a water-white solution on shaking; until this condition is attained, further small quantities of zinc oxide are added, if required, and the liquid heated. The precipitate must not contain much zinc, and must show the brown colour of ferric hydroxide; considerable excess of zinc oxide leads to low results. Any milkiness due to zinc oxide affects the end-reaction, and should be removed by the cautious addition of dilute hydrochloric acid. The liquid is then diluted to 400 c.c. (which is taken as the uniform volume for all titrations), heated to  $80^{\circ}$ , and standard permanganate added in quantities of 5 c.c. at a time until a red coloration persists on shaking. Suppose  $5 \times 5$  c.c. (= 25 c.c.) to have been required. The second portion of the solution is similarly precipitated and titrated by adding 20 c.c. of permanganate and completing the titration with 1 c.c. at a time, when, say, 23 c.c. are required. In the final solution, 22 c.c. of the standard solution are run in at once, and portions of 0.2 c.c. added until a red tint is attained equal to that produced by 0.1 c.c. of permanganate in 400 c.c. of water. It is well to have a flask of water thus coloured at hand; the tints are never quite the same, but can be equalised sufficiently for practical purposes. If, for example, 22.6 c.c. are required to reach this end-reaction, they are counted at 22.5 c.c. in calculating the result.

After each addition of the standard solution, the flask is well shaken and the contents allowed to settle sufficiently to show the colour of the supernatant liquid. This is facilitated by the use of the special stand shown in Fig. 5.

The three separate determinations, as described above, are only necessary if the manganese content is previously unknown; if the proportion is known approximately, two determinations, or even one, will suffice. When carried out as above, the method is fairly rapid.

The majority of other metals likely to occur in iron ores do not affect the accuracy of this method appreciably, as they are usually present only in small quantities. Copper is completely precipitated by



the zinc oxide as hydroxide. Nickel and lead are apt to cause high results when present in considerable quantity; cobalt and chromium, however, have this effect even when present in very small amounts. In order to remove cobalt, nickel, and lead, the hydrochloric solution of the ore is treated with an excess of ammonia and ammonium

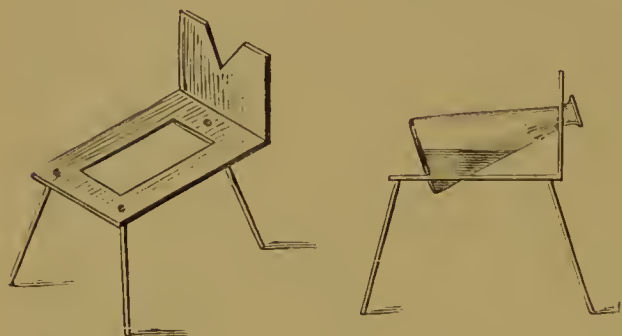


FIG. 5.

sulphide, and then rendered slightly acid with hydrochloric acid; after filtering, boiling, and oxidising with potassium chlorate, the solution is ready for the determination of the manganese. When chromium is present, it is best to precipitate all the manganese by the chlorate method (p. 61), dissolve

the washed peroxide in hydrochloric acid, boil, neutralise with zinc oxide, and titrate. Tungsten is oxidised to tungstic acid, and remains in the residue on filtration.

The following further methods have been proposed for the volumetric estimation of manganese:—

Low<sup>1</sup> dissolves 0.5 g. of ore in 10 c.c. of hydrochloric acid or aqua regia, evaporates nearly to dryness, adds 75 c.c. of hot water and excess of zinc oxide, boils, and treats with 25 to 50 c.c. of bromine water, according to the proportion of manganese present. The excess of bromine is boiled off, the precipitate filtered, washed, returned to the beaker, and dissolved in 50 c.c. of dilute sulphuric acid (1:9) with the aid of a known volume of oxalic acid or of ferrous ammonium sulphate solution. The excess of the latter is, after dilution, titrated back with permanganate.

Sarnström,<sup>2</sup> as well as Schöffel and Donath,<sup>3</sup> titrate manganous oxide in presence of alkali instead of acid. The latter dissolve the sample in hydrochloric acid, oxidise, evaporate, redissolve in water, and make up to a definite volume, and then transfer the liquid to a burette. Meanwhile a dilute solution of sodium carbonate is placed in a beaker, and as much standard permanganate solution added as is required to react with at least one-third of the manganese present in the sample. This mixture is then titrated with the original solution. Iron and alumina are precipitated as hydroxides, and the manganese as carbonate, which is oxidised by the permanganate. This method is easily carried out; according to C. Anger, however, it gives results which

<sup>1</sup> *J. anal. and applied Chem.*, 1892, 6, 663; *Chem. News*, 1893, 67, 162.

<sup>2</sup> *Stahl u. Eisen*, 1884, 4, 127; *Chem. News*, 1883, 47, 177.

<sup>3</sup> *Stahl u. Eisen*, 1883, 3, 374; *J. Iron and Steel Inst.*, 1883, p. 381.



are too low in proportion to the quantity of iron present, probably because the precipitated ferric hydroxide encloses traces of manganese carbonate, and thus withdraws them from reaction.

C. Meinecke<sup>1</sup> dissolves the ore in hydrochloric acid, oxidises with chlorate, boils, and treats with just enough zinc oxide to precipitate the iron. A known volume of standard permanganate—more than enough to react with the manganese present—is mixed in a 500 c.c. flask with 50 to 60 c.c. of zinc sulphate solution (1:2); to this the original solution is added in small quantities at a time, with thorough agitation, and the whole diluted to the 500 c.c. A portion of the solution is then filtered through an asbestos filter, 250 c.c. of the clear filtrate treated with 25 c.c. of antimony chloride solution (15 g.  $\text{Sb}_2\text{O}_3$  in 300 c.c. of hydrochloric acid of sp. gr. 1.19 made up to a litre) and 25 c.c. of hydrochloric acid, and titrated with permanganate. The relation of the antimony solution to the permanganate is fixed by a separate titration. Instead of antimony chloride, a solution of ferrous sulphate (100 g. with 25 c.c. of dilute sulphuric acid made up to 2 litres) may be used.

According to Schöffel and Donath,<sup>2</sup> in such a method as the above, the titration can be carried out just as well without filtering, *i.e.*, in presence both of ferric hydroxide and manganese peroxide. They prefer to titrate back the permanganate with arsenious acid, and in order to ensure the neutrality of the liquid, they introduce a little cream of zinc oxide before adding the arsenious acid solution.

Numerous methods have been worked out in which the manganese is separated as peroxide, and redissolved in presence of an excess of oxalic acid or ferrous sulphate, which is then titrated back. Such methods have been proposed by Hampe<sup>3</sup> and by Ukena<sup>4</sup>; that of the latter has been subsequently modified by Norris.<sup>5</sup> These methods are better adapted to the estimation of manganese in iron and steel than in ores, and will be described later in this connection (see p. 60). Myhlertz<sup>6</sup> fuses the ore with sodium carbonate and nitre, reduces the permanganate thus formed with alcohol, and determines the resulting peroxide by means of ferrous sulphate and standard permanganate. Moore<sup>7</sup> converts the manganese into the violet manganic metaphosphate and titrates with ferrous sulphate. Blum<sup>8</sup> titrates with potassium ferrocyanide in presence of ammonia, ammonium chloride, iron, and tartaric acid, whereby manganese ammonium ferrocyanide is precipitated; the

<sup>1</sup> *Stahl u. Eisen*, 1886, 6, 164; *J. Soc. Chem. Ind.*, 1887, 6, 457.

<sup>2</sup> *Stahl u. Eisen*, 1887, 7, 30; *J. Chem. Soc. Abstr.*, 1887, 52, 399; *J. Iron and Steel Inst.*, 1887, i., 469.

<sup>3</sup> *Chem. Zeit.*, 1883, 7, 73.

<sup>4</sup> *Stahl u. Eisen*, 1891, 11, 381.

<sup>5</sup> *J. anal. and applied Chem.*, 1892, 5, 430.

<sup>6</sup> *Ibid.*, 1891, 4, 267; *J. Chem. Soc. Abstr.*, 1891, 60, 366.

<sup>7</sup> *Chem. News*, 1891, 64, 66.

<sup>8</sup> *Z. anal. Chem.*, 1891, 30, 284; *J. Soc. Chem. Ind.*, 1891, 10, 798.

end-reaction is judged by the use of acetic acid as an external indicator, which gives a blue coloration with the least excess of soluble ferrocyanide.

**Chromium.**—A solution containing all the chromium as sodium or ammonium chromate is prepared as in the gravimetric method described on p. 17. After filtering and making up to 250 c.c., an aliquot part is titrated with ferrous ammonium sulphate (see Steel Analysis, p. 70).

**Vanadium.**—A small proportion of vanadium occurs in a variety of iron ores. For its estimation<sup>1</sup> 10 to 12 g. of the ore are dissolved in hydrochloric acid, any contained ferrous iron oxidised with nitric acid, an excess of which should be avoided, the solution filtered, and the filtrate treated as described on p. 75.

**Phosphorus.**—According to Emmerton's method, described fully by Blair,<sup>2</sup> phosphorus may be determined volumetrically in the phospho-molybdate precipitate by means of permanganate, according to the following reaction:—



The strength of the permanganate, in terms of iron, is multiplied by 0.01651 to give the phosphorus, or by 0.03781 to give phosphoric anhydride.

To carry out the determination, the yellow precipitate is thoroughly washed, the filter paper pierced, and the precipitate washed off and dissolved in dilute ammonia (1:4) in a 1000 c.c. flask; a large excess of ammonia should be avoided. Ten grams of granulated zinc and 800 c.c. of warm dilute sulphuric acid (1:4) are then added and the flask warmed for ten minutes, without boiling, on a sand-bath. A change of colour is observed as the molybdic acid is reduced to the oxide,  $\text{Mo}_{12}\text{O}_{19}$ , the final tint being a dark olive green. The liquid is poured through a large pleated filter, the residue washed once with cold water, and the washings poured through the filter paper. The filtrate, which becomes a yellow colour, owing to the action of the air, but which is not appreciably oxidised, is then titrated with permanganate; shortly before complete oxidation it becomes colourless, so that the change to pink is observed without difficulty.

**Sulphur.**—The following method, originally due to Watson<sup>3</sup> and modified by Lunge,<sup>4</sup> for the estimation of sulphur in pyrites cinders is applicable (*cf.* Vol. I., 294-6). About 3.2 g. of substance are mixed with exactly 2 g. of sodium bicarbonate, the alkalinity of which has been determined by titration. The mixture is heated in a 20 c.c. nickel crucible, at first quite gently, so that the tip of the flame just touches

<sup>1</sup> *Cf.* Campagnac, *Ber.*, 1903, 36, 3164.

<sup>2</sup> *The Chemical Analysis of Iron*, p. 92.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1888, 7, 305.

<sup>4</sup> *Z. angew. Chem.*, 1892, 5, 447; *J. Soc. Chem. Ind.*, 1893, 12, 292.

the bottom of the crucible, for ten to fifteen minutes, then to a full red heat for twenty minutes. The mass must not be allowed to fuse. To avoid mechanical loss, the crucible is kept covered and the contents are not stirred during the preliminary heating, but are stirred frequently during the ignition at the higher temperature. After cooling, the cake, which should be black and quite porous, is transferred to a porcelain dish and lixiviated with boiling water. If, as sometimes happens, the solution filters with difficulty, it is advisable to add a concentrated solution of sodium chloride accurately neutralised with hydrochloric acid in presence of methyl orange, to moisten the filter paper with the same solution, and to agitate the liquid in the filter during filtration. After repeating the extraction several times and washing with sodium chloride solution, the clear united filtrates are titrated back with  $N/5$  hydrochloric acid and methyl orange.

### 3. DRY ASSAYS

Generally speaking, the dry assays at one time in use in the iron and steel industry are far less accurate than the wet ones, and are, therefore, deservedly obsolete. One or two dry tests, however, are still in use for iron ores. The so-called German assay, for instance, aims at reproducing the effects of blast furnace smelting. The ore is ignited, with the requisite admixtures, in a carbon-lined crucible, and the resulting regulus of iron is detached and weighed. The mixing should be exactly the same as for a blast furnace charge, and be based upon a previous analysis of the ore; the regulus will then contain the corresponding amounts of silicon, carbon, manganese, etc. In this way the approximate yield of pig iron is ascertained and information is gained as to the behaviour of the ore in smelting. The test is largely used in Sweden; details of the method are given in the handbooks of Balling,<sup>1</sup> Kerl, and others.

**The Reducibility Test.**—A second dry test, which has only come into use recently, is the reducibility test. It is of great importance, in organising the blast furnace process, to know the behaviour of an ore towards reducing agents. A method has been worked out by Wiborgh<sup>2</sup> by means of which this property may be determined quantitatively.

Ores which are reduced by carbon monoxide are considered easily reducible, whilst those which are only reducible by carbon are considered difficult of reduction. The degree of reducibility depends on the content of oxygen and on the density of the ore, and is roughly proportional directly to the former and inversely to the latter. Hence,

<sup>1</sup> C. M. Balling, *Die Probierkunde*, 1879.

<sup>2</sup> *Stahl u. Eisen*, 1887, 17, 804; *Chem. News*, 1898, 78, 4.



for the complete valuation of an ore chemical analysis does not provide all the data, but is advantageously supplemented by a reducibility test. The test consists of two operations, the reduction of the ore and the chemical examination of the products formed.

The reducing apparatus consists of a cylindrical gas-producer (Figs. 6 and 7) of 25 cm. diameter and 1.2 m. height, in the centre of which is fixed an iron tube of 50 mm. bore. A sample of ore is suspended within the latter and reduced with carbon monoxide, which

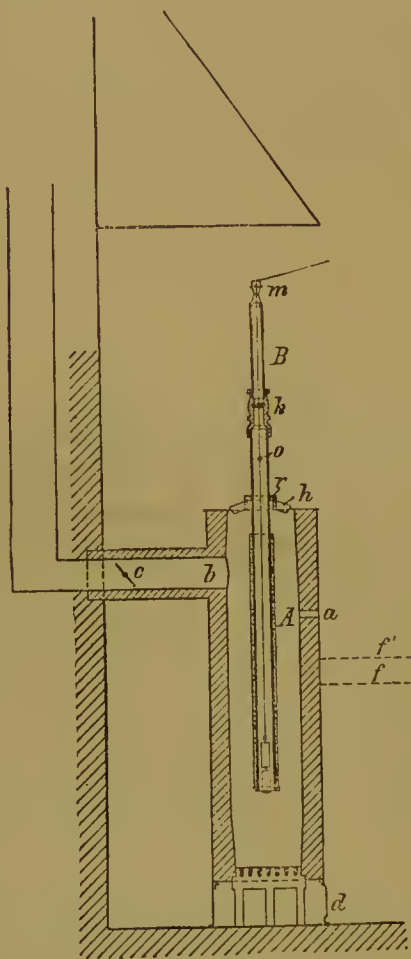


FIG. 6.

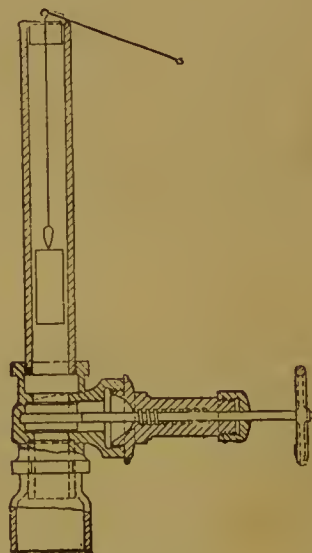


FIG. 7.



FIG. 8.

is produced by the combustion of charcoal. The inner tube is protected by a covering of fire-clay, which is wired on and is connected at the upper end with an adapter containing a valve, and is prolonged upwards by a tube of 33 mm. bore. The total length of the reduction tube is 1.6 m., and the lower end hangs 25 cm. above the grid of the outer tube.

In conducting a test, 8 to 10 g. of the ore, passed through a sieve of 19 meshes to the sq. cm., are introduced into a cage of wire gauze of the shape and section shown in Fig. 8, and let down by a wire into the reduction tube. Three cages, separated by pieces of



foil, may be treated simultaneously. The charge is exposed to the action of carbon monoxide, at that point of the tube where the temperature is  $400^{\circ}$ , for one hour, and then for a further hour at the bottom end of the tube. According to Wiborgh, the temperature gradient is as follows:—

Distance from top.	Temperature.
500 mm.	$400^{\circ}$
900 „	$525^{\circ}$
1200 „	$700^{\circ}$
1500 „	$800^{\circ}$ to $880^{\circ}$

The reducing gas contains 3 to  $3\frac{1}{2}$  per cent. of carbon dioxide and 30 to 32 per cent. of carbon monoxide. After reduction, the sample is allowed to cool in a current of the reducing gas.

*Analysis of the Reduced Ore.* Under the above conditions, the ore will be reduced partly to iron and partly to the oxide  $\text{Fe}_6\text{O}_7$ , whilst a certain amount of carbon will be deposited on it. The following analytical determinations are then made:—(1) carbon; (2) total iron; (3) metallic iron; and (4) the degree of oxidation.

1. *Carbon.* This is determined by the chromic acid method, as in steel analysis (p. 49).

2. *Total Iron* is determined as in the original ore, by one of the volumetric methods as described above.

3. *Metallic Iron.* For this estimation the hydrogen evolved by the

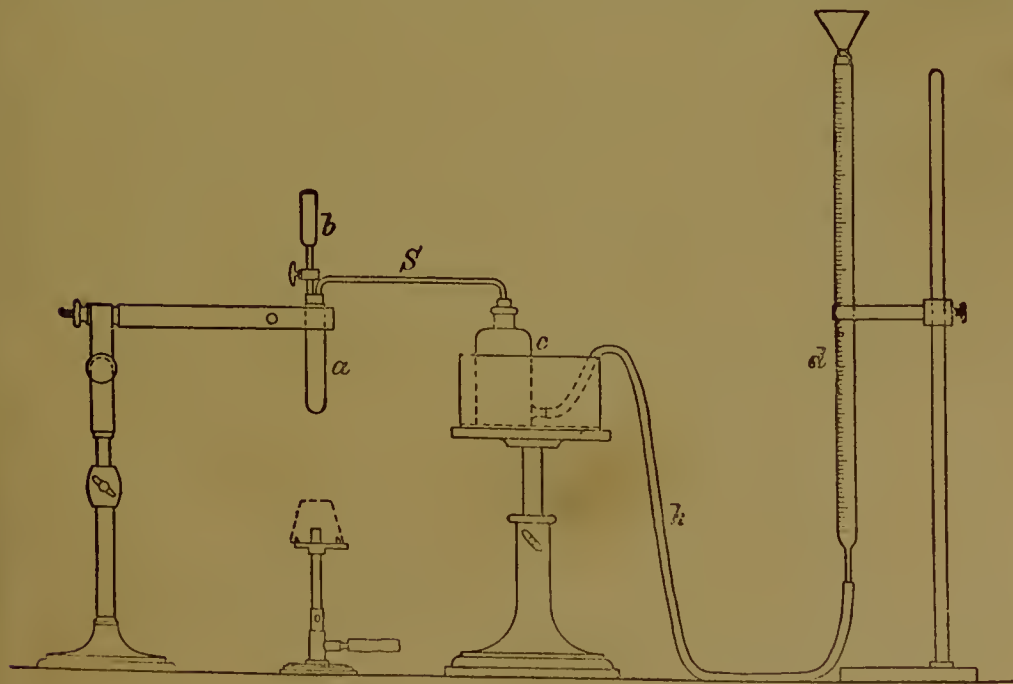


FIG. 9.

action of dilute sulphuric acid is measured. From 0.2 g. to 1.0 g. of substance is weighed into a test tube *a*, (Fig. 9), and covered with a few cubic centimetres of water. The test tube is fitted with a rubber stopper

provided with a dropping-funnel *b*, and an exit tube *S*, which leads to a Woulff's bottle, *c*, of 200 c.c. capacity, filled to four-fifths with very dilute potassium hydroxide solution to absorb any carbon dioxide that may be evolved; the lower tubulure is connected by rubber tubing with the burette *d*. The apparatus having been fitted up, *a* is warmed to 20° by means of a beaker containing water at this temperature, atmospheric equilibrium established by raising or lowering *d* to the level of *c*, and the meniscus in the former read off. It is well to displace *d* for some minutes and take a second reading, in order to make sure that the apparatus is gas-tight. Exactly 10 c.c. of dilute sulphuric acid (1 : 8) are then dropped upon the substance from *b* when hydrogen begins to be evolved. After an hour's action at the ordinary temperature, the vessel is gently heated up to boiling, until no more gas comes off. During this evolution of the hydrogen, *d* is gradually lowered so as to keep approximately the atmospheric pressure. The bottle *c* is kept in a vessel containing water, and should remain at 20° from start to finish. Finally, *a* and its contents are cooled to 20°, the levels in *c* and *d* equalised, and the level in *d* again read off; this gives the volume of evolved hydrogen, plus 10 c.c. (the volume of the acid added).

According to the equation—



1.0 g. Fe yields 401.2 c.c. of hydrogen at 0° and 760 mm. The volume of gas found is reduced to normal conditions and divided by 401.2; the quotient gives the amount of metallic iron in the sample.

4. *The Degree of Oxidation.* The data required to ascertain the degree of oxidation are, besides those furnished by the estimations (2) and (3), the content of ferrous oxide in the original ore, and the content of metallic iron plus ferrous oxide in the reduced ore. This latter is determined by dissolving a portion in absence of air (*cf.* p. 33) and titrating.

If the highest oxide of iron,  $\text{Fe}_2\text{O}_3$ , be supposed to have the degree of oxidation 100, then the oxides have the following degrees:—

3 $\text{Fe}_2\text{O}_3$	=	$\text{Fe}_6\text{O}_9$	.	.	.	100
3 $\text{Fe}_2\text{O}_3 - \text{O}$	=	$\text{Fe}_6\text{O}_8$	.	.	.	88.9
3 $\text{Fe}_2\text{O}_3 - \text{O}_2$	=	$\text{Fe}_6\text{O}_7$	.	.	.	77.8
3 $\text{Fe}_2\text{O}_3 - \text{O}_3$	=	$\text{Fe}_6\text{O}_6$	.	.	.	66.7

If, as the result of the analytical determinations, say *n* per cent. of total iron, *m* per cent. of iron as metal and ferrous oxide, and *r* per cent. of metallic iron, have been found, then the degree of oxidation, *x*, will be, in the case of the original ore:—

$$n \frac{3}{2} : (n - m) \frac{3}{2} + m = 100 : x,$$

$$\text{or} \quad x = \left(1 - \frac{m}{3n}\right) 100;$$

and in the case of the reduced ore :—

$$(n-r)\frac{3}{2} : (n-r) - (m-r)\frac{3}{2} + (m-r) = 100 : x,$$

$$\text{or} \quad x = \left(1 - \frac{m-r}{3(n-r)}\right)100.$$

5. *The Degree of Reducibility* of an ore is expressed as the ratio of metallic iron in the reduced ore to the total iron in the original ore, multiplied by 100.

## II.—ANALYSIS OF IRON AND STEEL

All varieties of iron and steel invariably contain iron, carbon, silicon, and manganese as normal constituents. They may further contain sulphur, phosphorus, copper, nickel, arsenic, and titanium by way of impurities. In most cases traces of calcium, magnesium, aluminium, cobalt, lead, antimony, nitrogen, etc., may be shown to be present; but they occur in such minute quantities as not to influence the properties of the metal perceptibly, and are therefore hardly ever determined. The estimation of chromium, tungsten, nickel, vanadium, and molybdenum is of importance, since these metals occur as essential components of certain steels and of the alloys employed in making them. As a rule, the constituents of an iron and steel are known beforehand, so that qualitative analysis is generally superfluous. It may happen, however, that one of the four last-named metals has to be tested for, or perhaps titanium or arsenic. The methods to be adopted in these circumstances follow either from the remarks on the testing of iron ores or from the quantitative methods described below.

### QUANTITATIVE ANALYSIS

**Sampling.**—The taking of samples of wrought iron or of grey cast iron for analysis is a comparatively simple matter. The metal is best comminuted by drilling, planing, or turning, to the degree of fineness required. In the absence of machinery for this purpose, the metal may be clamped in a vice and reduced to filings by means of a rasp, the filings being caught on a sheet of clean paper. To minimise contamination with the substance of the rasp, this should be as hard as possible, but not so brittle that portions of the teeth are snapped off. White cast iron and the hardest kinds of steel may be dealt with by means of tools made of special steels; when, as is often the case, such tools are not at hand, pieces should be chipped off the metal with a large hammer and then pounded in a specially hardened steel mortar. The fragments are sifted through a sieve of  $\frac{1}{2}$  mm. mesh and the residue again pounded

up; this is repeated until the whole has passed through the sieve. Cast steel blocks, which are never homogeneous, should preferably be sampled after they have been forged or rolled. Cast irons also are never quite homogeneous, and the pig or casting should be sampled at several points.

A special difficulty arises in the case of grey cast iron, from which, on drilling or filing, grains of graphite are detached and tend to segregate themselves from the specifically heavier iron. This may lead to errors in the carbon determinations up to 0.2 per cent. One remedy consists in sifting off the graphite and weighing out fine and coarse samples separately, in the original proportions, every time. Or, the whole sample may be thoroughly shaken up in a stoppered bottle with a little alcohol. When a portion is required for analysis, a sufficient quantity, as judged by the eye, is withdrawn, dried, and then weighed. It is hardly possible to obtain an absolutely representative sample of grey cast iron, but the only determination in which this disadvantage makes itself felt to any extent is that of carbon.

**Silicon.**—1. *Evaporation Method.* The quantity weighed out for analysis should be varied according to the probable content of silicon—*e.g.*, 1 g. of grey pig or cast; from 2 to 3 g. of white; and from 3 to 5 g. of malleable iron or steel. The metal is dissolved in nitric acid, evaporated to dryness, taken up with hydrochloric acid, and the solution diluted and filtered. The residue is fused with fusion mixture, and the melt evaporated to dryness with excess of hydrochloric acid. On extracting with water, filtering, and igniting, the silica is obtained pure, and is then weighed.

This twofold evaporation is somewhat tedious, and is adopted in order that the silica may ultimately be free from iron. The method, therefore, though troublesome, gives accurate results.

When the siliceous residue obtained in the first operation is not very highly ferruginous, the further purification may be circumvented as follows:—The impure silica is ignited and weighed; it is then evaporated with hydrofluoric acid and a few drops of sulphuric acid, ignited, and weighed again; the difference between the two weighings represents the silica. If the residue is considerable, it is advisable to treat it with ammonium carbonate so as to make sure that all sulphuric acid is completely volatilised.

2. *Blum's Method.*<sup>1</sup> The metal is dissolved in hydrochloric acid containing bromine, and evaporated to dryness, after addition of twice its weight of ammonium chloride, whereby the drying is facilitated. The residue, after lixiviation, is washed on the filter alternately with water and with hydrochloric acid containing bromine. The silica is thus obtained of a pure white colour, and leaves no residue on treatment with hydrofluoric acid.

<sup>1</sup> *Stahl u. Eisen*, 1885, 5, 594; *Chem. News*, 1886, 53, 300.



3. *Drown's Method*.<sup>1</sup> The metal is dissolved in nitric acid of sp. gr. 1.2. When all action has ceased, about 25 to 30 c.c. of dilute sulphuric acid (1:3), or 35 to 40 c.c. of 1:4 acid (Ledebur), are added and evaporated on a sand-bath or hot-plate until all the nitric acid is expelled and copious white fumes of sulphur trioxide are evolved. The cooled residue is lixiviated with 100 c.c. of water, warmed till the ferric sulphate has gone into solution, and filtered. The mixture of carbon and silica on the filter is thoroughly washed with hot water, then with four successive portions of hot hydrochloric acid (sp. gr. 1.12), and finally with hot water. After ignition the silica should be pure white in colour; ignition for two to three hours at a full red heat may be necessary with cast irons, etc., if much graphite be present.

This method is the one usually adopted in works' laboratories. A modification suggested by Strick<sup>2</sup> consists in evaporating down the metal with dilute sulphuric acid alone, in a beaker; when a cold clock-glass laid on the beaker shows that no more water vapour is being evolved, the residue is lixiviated and proceeded with as above.

Ferro-silicon is in some cases resistant both to nitric acid and to hydrochloric acid containing bromine. It is then necessary to mix 0.2 to 0.3 g. with fifteen times its weight of sodium carbonate and sodium peroxide mixture (1:2) in a nickel crucible and very gradually heat to fusion, when the alloy is readily decomposed. The melt is then extracted and evaporated with hydrochloric acid.

Brearly and Ibbotson<sup>3</sup> give the following method for the determination of silicon in ferro-silicons, which gives excellent results (Lambert). Two grams of the finely ground sample are dissolved in 50 c.c. of concentrated hydrochloric acid, to which is added 10 to 20 c.c. of nitric acid, the solution boiled for not less than fifteen minutes, made up with water to 200 c.c. and filtered without delay. The residue is washed with cold dilute hydrochloric acid, ignited strongly for at least thirty minutes, and then allowed to cool in the desiccator and weighed quickly. If this method be accurately followed, an addition of 0.1 per cent. as a correction for the soluble silica will give results more nearly approximating the actual silicon content than even more elaborated methods (Lambert).

It is to be noted that all these methods make no distinction between silicon combined with iron and silica present in the form of enclosed slag. The point is of little technical importance, but in scientific investigations the determination of silicon proper may be called for. This is done, according to both Watts<sup>4</sup> and Turner,<sup>5</sup> by igniting in a current of chlorine, collecting the vaporised ferric chloride and silicon

<sup>1</sup> *Chem. News*, 1880, 42, 299; 1884, 60, 20.

<sup>2</sup> *Stahl u. Eisen*, 1886, 6, 510.

<sup>3</sup> *The Analysis of Steel Works' Materials*, p, 117.

<sup>4</sup> *Stahl u. Eisen*, 1882, 2, 444; *Chem. News*, 1882, 45, 279.

<sup>5</sup> *Chem. News*, 1884, 49, 233.

tetrachloride in water, evaporating the solution, and igniting and weighing as usual. Any enclosed slag or cinder is thus left behind in the boat, and may be collected, examined, and weighed.

**Titanium.**—Titaniferous ores generally yield pig iron containing this metal; refined iron and steel, however, are generally free from it. Ferro-titanium alloys are occasionally specially prepared.

The older method of determining titanium is based on the precipitation of titanium dioxide from solutions in sulphuric acid by prolonged boiling. In the case of pig iron, 5 to 10 g. of the metal are dissolved in hydrochloric acid, evaporated to complete dryness, taken up with dilute acid, and filtered. The insoluble residue is ignited, evaporated with hydrofluoric acid and a little sulphuric acid, and fused with acid potassium sulphate. The melt is dissolved in cold water and added to the ferric chloride solution, which is then evaporated down with sulphuric acid until all the hydrochloric acid is expelled; the residue is taken up with water, and reduced by means of sulphur dioxide or sodium sulphite. The solution thus obtained is nearly neutralised with sodium carbonate and boiled in a covered beaker for two hours, the vaporised water and sulphurous acid being replaced from time to time. Titanium dioxide, phosphoric acid, and a little iron are thus thrown down and filtered off; the filtrate is tested for phosphoric acid by further boiling. The precipitate is fused with sodium nitrate and carbonate, and the melt extracted with water, which leaves sodium titanate and ferric oxide undissolved, whilst the sodium phosphate goes into solution. The residue is dissolved in sulphuric acid, reduced, and boiled as before. The titanium now comes down as a pure white precipitate, and is filtered off, ignited, and weighed. Ignition with ammonium carbonate ensures complete removal of sulphuric acid.

According to Baskerville,<sup>1</sup> titanium dioxide is precipitated from a neutral ferric chloride solution on boiling, after reduction with sulphur dioxide. It would, therefore, seem feasible to omit the conversion into sulphate.

Ledebur<sup>2</sup> found that a large excess of iron chlorides prevents the titanium from being completely precipitated; to overcome this, he adopted the following method of estimation. The silica having been rendered insoluble by evaporation to dryness, the residue is taken up with dilute hydrochloric acid, and the filtered solution, after concentration, is twice shaken out with ether (*cf.* p. 9). The resulting aqueous solutions, from which titanium may already have begun to settle out, are united and evaporated to dryness; when the residue is taken up with dilute hydrochloric acid, titanium dioxide, in a pure condition, remains undissolved. This method is less tedious than the above, older process.

<sup>1</sup> *J. Amer. Chem. Soc.*, 1894, 16, 427.

<sup>2</sup> *Stahl u. Eisen*, 1894, 14, 810.

The method most frequently adopted in technical laboratories consists in dissolving about 5 g. of the sample in hydrochloric acid, and, when evolution of hydrogen is no longer apparent, diluting to about 250 c.c. with water. The solution is then rendered neutral with ammonia, any traces of iron being dissolved by the addition of a drop or two of dilute hydrochloric acid. Ten to twelve grams of sodium thiosulphate are then added and the whole gently boiled on a hot-plate for twenty minutes. The ignited precipitate is then purified after treatment with hydrofluoric and sulphuric acids, if necessary, by fusion and reprecipitation, or is estimated colorimetrically (Lambert).

Ferro-titanium does not dissolve readily in acids. It may be decomposed by distributing 0.5 g. of the finely divided alloy upon the cooled, fused surface of 10 g. of acid potassium sulphate contained in a large platinum crucible. The contents of the crucible are then heated and the temperature maintained "until no gritty particles can be felt with a stout platinum wire" (Brearly and Ibbotson). The mass, when cold, is digested with water. Ten c.c. of sulphuric acid are then added and the solution gently heated. The titanium is precipitated from the filtered solution by boiling with sodium thiosulphate.

G. W. Wdowischewski<sup>1</sup> has proposed the following method for the estimation of titanium in ferro-titanium. The alloy is dissolved in moderately dilute sulphuric acid, the solution treated with nitric acid, and after filtering off the silica, tartaric acid and ammonia are added. The iron is then precipitated with hydrogen sulphide, filtered off, the tartaric acid in the filtrate decomposed by addition of more nitric acid, and heating, and then ammonia added to the colourless solution, when the titanic acid is precipitated in the form of white flakes free from iron.

Titanium dioxide, when free from iron, may be conveniently estimated colorimetrically, owing to its property of giving a fine orange colour with hydrogen peroxide in sulphuric acid solution. The standard is prepared by adding to a solution containing 1 mg. of  $\text{TiO}_2$  per c.c. an equal volume of hydrogen peroxide, so that the resulting liquid contains 0.5 mg. per c.c. Schneider<sup>2</sup> proposes to determine titanium in one operation before precipitating the aluminium (*cf.* p. 68). The iron is removed by means of ammonium sulphide, the filtrate evaporated to dryness, fused with sodium carbonate, and taken up with sulphuric acid; the titanium is then estimated colorimetrically in this solution.

The application of this method is, however, somewhat limited, as molybdenum, vanadium, and chromium interfere with the colorimetric estimation of the titanium, as do also nickel and copper if present (Lambert).

<sup>1</sup> *Eng. and Min. J.*, 1908, 85, 1200.

<sup>2</sup> *Oesterr. Zeitschrift*, 40, 471.



**Carbon.**—So far as is at present known, carbon can occur in iron in four modifications. Two of these—*graphite*, which is crystalline and rarely found in steels, and is confined almost entirely to cast iron, and *temper-carbon*, which is amorphous and behaves like graphite, in that it is not acted upon by boiling hydrochloric or nitric acid—are present in mechanical admixture with the metal. *Carbide-carbon* is present in definite chemical combination as a carbide of iron; whilst the fourth modification, *hardening carbon*, is present in the iron as an iron-carbon alloy.

Graphite and temper-carbon may be determined together, or the former may be determined alone. It is also possible to determine carbide-carbon by itself. Hardening carbon can only be determined by difference. Usually, the estimation of carbon in refined iron and steel is limited to a determination of the total carbon.

**Total Carbon.**—There are numerous methods for estimating total carbon, but in almost all cases the carbon is ultimately determined as carbon dioxide. The procedure may consist either in oxidising the metal directly by combustion either in the dry or in the wet way, or in previously removing the iron by solution or volatilisation and then combusting the residue.

1. *Direct Dry Combustion Method.* The oxidising medium may be either free oxygen alone, or free oxygen in conjunction with oxidising admixtures such as chlorates or chromates, or metallic oxides such as cupric oxide, or else indifferent agents such as alumina, magnesia, etc.

The metal, in the form of either small shavings or filings, is placed, with or without admixtures, in a platinum or porcelain boat, and introduced into a heated porcelain tube the front end of which is charged with copper oxide. Tubes of clear quartz, wound with wire or foil for electrically heating, may be employed with advantage where current is available.<sup>1</sup> Suitable apparatus for purifying and drying the supplies of air and oxygen are attached to the inlet side of the tube, and the other end is connected with a series of cooling and drying-tubes, the apparatus for absorbing the evolved carbon dioxide, and a final guard-tube containing hygroscopic material. All the connections having been made secure, the combustion tube is heated to a bright red heat and a current of air passed through, followed by a current of oxygen. The regulation of the temperature requires care, since a certain minimum temperature is necessary for reasonably rapid combustion of the carbon, whilst over-heating leads to the formation of molten ferroso-ferric oxide, which may cover the particles of iron, and thus prevent their oxidation. Hence, the general tendency of this method is to give low results, owing to incomplete combustion. According to Schneider,<sup>2</sup> the process is greatly facilitated and requires

<sup>1</sup> Cf. *Analyst*, 1909, 34, 88.

<sup>2</sup> *J. Iron and Steel Inst.*, 1894, ii., 488.



only moderate temperatures, if 3 g. of the iron are mixed with 10 g. of certain metallic powders (*e.g.*, three parts of lead to one of copper), or with the same quantity of powdered phosphor-copper. Similarly, potassium bichromate, or a mixture of potassium chlorate and lead chromate, or copper oxide, are employed to facilitate the oxidation.

Direct igneous combustion is a process requiring considerable experience, but is particularly applicable; in general, it is mainly confined to iron alloys which are difficult to decompose with acids, such as silicon, tungsten, chromium, and molybdenum alloys. A number of modifications of the method have been proposed. Lorenz<sup>1</sup> uses an injector furnace and subjects the tube at a white heat to such a temperature that the oxide becomes quite liquid and slags off. Pettersson and Smith<sup>2</sup> combust, in presence of molten acid potassium sulphate, retain the sulphur dioxide with chromic acid, and absorb the carbon dioxide with baryta solution, the excess of which is subsequently titrated back. Förster<sup>3</sup> combusts, without the use of oxygen, by heating with lead chromate in a porcelain retort. Mercuric oxide is also used in this way.

2. *Direct Wet Combustion Method.* The iron is oxidised by boiling with a mixture of chromic and sulphuric acids (Gmelin<sup>4</sup> and v. Jüptner<sup>5</sup>); the evolved gases may be further oxidised by igneous combustion (Särnström). Objections have been raised to this method (Wedding<sup>6</sup>), but nevertheless it is one of the most accurate, and takes comparatively little time to carry out. It is applicable to all kinds of iron and iron alloys except ferro-silicon and ferro-chrome. The following standard procedure was worked out by Corleis.<sup>7</sup>

The apparatus (Fig. 10) consists of a purifying cylinder A, a boiling flask B, a combustion tube C, packed with copper oxide, and three U-tubes. The first of these, D, is a drying tube, and is charged with glassy phosphoric acid; the two others, E<sub>1</sub> and E<sub>2</sub>, serve for the quantitative absorption of the carbon dioxide, and contain soda-lime, with a short layer of glassy phosphoric acid at the exit end. The series is terminated by a small wash-bottle F, containing sulphuric acid, which serves both to prevent access of moist air to E and to show the rate of passage of the gases through the apparatus. The soda-lime tubes should have hollow ground-in stoppers; for the phosphoric acid, plain U-tubes, sealed off at the upper ends, are preferable. In order to save

<sup>1</sup> *Z. angew. Chem.*, 1889, 2, 395; *J. Chem. Soc. Abstr.*, 1893, 64, 291; 1894, 66, 119.

<sup>2</sup> *Ber.*, 1890, 23, 1401; *J. Iron and Steel Inst.*, 1890, ii., 852; *Z. anal. Chem.*, 1893, 32, 385; *J. Iron and Steel Inst.*, 1893, ii., 527.

<sup>3</sup> *Z. anorg. Chem.*, 1895, 8, 274; *J. Iron and Steel Inst.*, 1895, ii., 588; *Cf. also* T. E. Hull, *Proc. Chem. Soc.*, 1910, 26, 61.

<sup>4</sup> *J. Iron and Steel Inst.*, 1883, p. 779.

<sup>5</sup> *Ibid.*, 1885, p. 246.

<sup>6</sup> *Eisenhüttenkunde*, 2nd ed., p. 611.

<sup>7</sup> *Stahl u. Eisen*, 1894, 14, 587.

phosphoric acid, the introduction of a sulphuric acid absorption vessel between C and D is sometimes adopted.

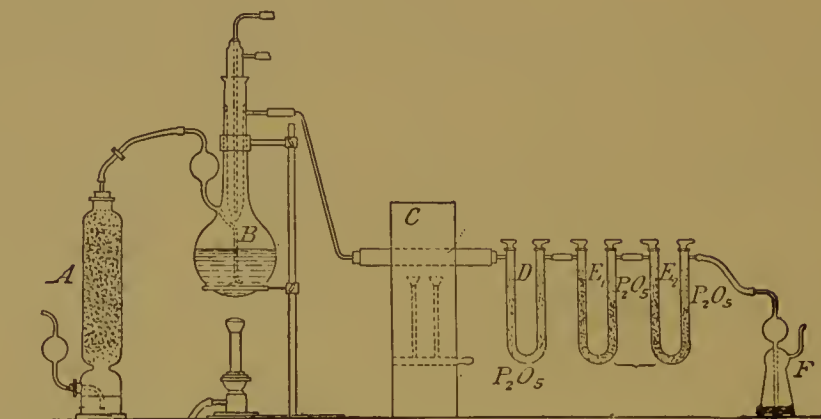


FIG. 10.

The most important part of the apparatus is the flask B, of which details and measurements are given in Fig. 11. A condenser *a* is ground into the neck *b* of the flask, which is widened out at *c* so as to provide a water-lute. A tube, reaching nearly to the bottom, is fused into the side of the flask; this is fitted with a bulb, as a safeguard against sucking back, and with a stoppered thistle funnel for introducing the liquid reagents; it must not be less than 6 mm. in bore, since it has a tendency to be blocked up with solid matter. The charge of metal is introduced into the flask either by means of a glass bucket *e*, suspended from a platinum wire, or through a wide funnel *d*.

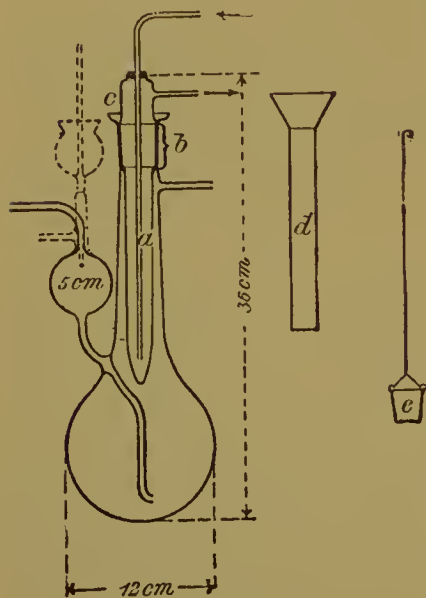


FIG. 11.

A mixture of 25 c.c. of saturated chromic acid solution, 150 c.c. of copper sulphate solution (200 g. to the litre), and 200 c.c. of concentrated sulphuric acid is the oxidising reagent employed. To carry out a determination, the liquids are filled into the flask in the order named, shaken up, cautiously heated to boiling and kept in brisk ebullition for ten minutes, the condenser being in position and supplied with running water. The flame is then removed, the purifying cylinder A connected up, and a gentle current of air sucked through for ten to twenty minutes. Next, the combustion and absorption tubes are attached and air again drawn through for five minutes. The absorption tubes are then closed, disconnected, laid in the balance case for ten minutes, momentarily opened

and closed again, wiped with wash-leather or silk, laid by for another five minutes, and weighed. By this time the oxidising mixture in the flask will have cooled down. The absorption tubes are replaced in position, the charge of metal let down into the flask, the lute at *c* made either with water or with sulphuric acid, and the liquid cautiously warmed up.

From 0.5 to 5 g. of metal is weighed out, according to the content of carbon. During the oxidising process a very gentle current of air is aspirated through the apparatus. The flame should be so regulated that the contents of the flask are brought to boiling in from fifteen to twenty minutes. Brisk boiling is then kept up for from one to two hours, according to the quantity and nature of the sample, the flame then removed, and about 2 litres of air drawn through. The absorption tubes are now closed, disconnected, and weighed with the precautions described above.

Experiment has shown that when copper sulphate is present, the

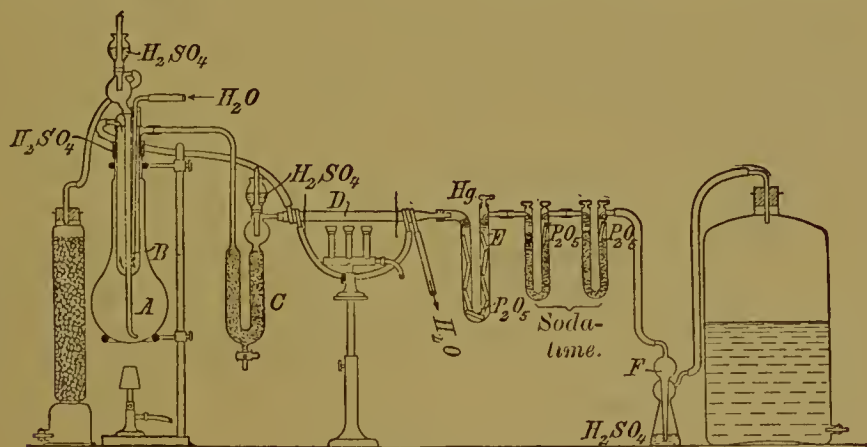


FIG. 12.

amount of carbon evolved as hydrocarbons is tolerably uniform for all classes of metal; it corresponds to about 2 per cent. of the total carbon. Consequently, for certain classes of routine analyses, the combustion tube can be dispensed with and the loss of carbon allowed for. It is convenient in this case to weigh out 2.77 g. instead of 2.7272 g., or 5.54 g. instead of 5.4544 g.; each 0.01 g. of carbon dioxide then indicates 0.1 per cent. or 0.05 per cent. respectively, of total carbon. When the combustion tube is absent, the U-tubes recommended by Corleis, which have obliquely placed tubulures, may be advantageously used, as the whole apparatus is then much more compact.

A simplified boiling flask is constructed by leading the supply-tube through the condenser, which is placed outside the flask. Perhaps the best modification proposed is that of Wüst,<sup>1</sup> shown in Fig. 12. The supply-tube runs through the condenser, but the condenser hangs inside the flask; the ground-glass junction is worked, not upon the water-

<sup>1</sup> *Stahl u. Eisen*, 1895, 15, 389.



jacket of the condenser, but upon an outer mantle; the height of the water-lute is thus increased to 3 to 4 cm. This arrangement has the great advantage that the flask proper can be withdrawn downwards for filling and emptying without disturbing any of the rubber connections. The drying tube C is charged with glass beads moistened with sulphuric acid, and is so designed that the acid can be replenished *in situ*. The position of the drying tube in front of the combustion tube, as here shown, is not, however, to be recommended. Ledebur found that the evolved gases impart to the acid a decided smell, resembling that of aldehyde, from which it would appear that a part of the carbon, which is liberated as hydrocarbons, is retained. The combustion tube employed by Wüst is made of platinum and is cooled by water at either end; this is more readily heated up than glass, and, of course, less liable to crack.

Details of the method, and also of the apparatus for the conduct of this process as carried out at the works of Messrs Cammell, Laird & Co. of Sheffield, have been published by Brearly and Ibbotson.<sup>1</sup>

3. *Preliminary Separation of Carbon, followed by the Wet Combustion Method.* Many reagents have been suggested for dissolving out the iron and leaving the carbon behind; the separation is, however, in most cases incomplete, with the exception of the methods in which copper sulphate or copper ammonium chloride is employed.

The method of separation by *Solution in Copper Sulphate* as originally worked out by Särnström, is generally recommended as accurate, as a result of the investigations of Lunge and Marchlewski, Ledebur, Wiborgh, and others. Lunge<sup>2</sup> employs the following six reagents for the estimation:—

1. Copper sulphate, saturated solution.
2. Chromic acid, 100 g. to 100 c.c. of water.
3. Sulphuric acid, sp. gr. 1·65, saturated with chromic acid.
4. Sulphuric acid, sp. gr. 1·71, saturated with chromic acid.
5. Dilute sulphuric acid, sp. gr. 1·10.
6. Hydrogen peroxide.

The proportions of these ingredients, and the amount of metal to be weighed out, are given in the following table:—

Carbon. per cent.	Weight of Samples. g.	Copper Sulphate Solution. c.c.	Chromic Acid Solution. c.c.	Sulphuric Acid. Spec. Grav.			Hydrogen Peroxide. c.c.
				1·65 c.c.	1·71 c.c.	1·10 c.c.	
Above 1·5 .	0·5	5	5	135	...	30	1
1·5 to 0·8 .	1	10	10	130	...	25	2
0·8 „ 0·5 .	2	20	20	130	...	5	2
0·5 „ 0·25 .	3	50	45	...	75	5	2
Below 0·25 .	5	50	50	...	70	5	2

<sup>1</sup> *The Analysis of Steel Works' Materials*, p. 11.

<sup>2</sup> *Stahl u. Eisen*, 1891, II, 666.



The apparatus used for the determination is the same as that described above. The metal is placed in the flask and dissolved in the cold by means of copper sulphate, with frequent agitation. The time required is at least six hours for pig iron and at least one hour for refined iron, etc.

When the reaction is ended, the condenser is inserted, the purifying, combustion, and absorption tubes connected up, and the other reagents introduced in the order:—chromic acid, strong sulphuric acid, and dilute sulphuric acid. Air is then drawn through and heat gently applied. When the first effervescence has subsided, the contents of the flask are kept simmering for half an hour. The flame is then removed and hydrogen peroxide slowly dropped in; the resulting evolution of oxygen expels all the carbon dioxide. Finally, about a litre of air is drawn through the apparatus.

*Solution in Copper Ammonium Chloride.* Copper ammonium, or copper potassium chloride, is an excellent solvent of iron, and was originally proposed by McCreath. The method of separating carbon by this reagent, filtering off, and combustion in oxygen is very generally practised both in England and in America, and is generally regarded as the usual procedure. Some doubts, however, have been thrown on its accuracy, especially as regards the older methods of working.<sup>1</sup>

The solvent is made up by dissolving 300 g. of neutral copper ammonium chloride to the litre, and may be very slightly acidulated with hydrochloric acid; 50 c.c. are required for 1.0 g. of metal. The sample is placed in a conical flask, the requisite proportion of the solvent added, and the whole thoroughly agitated, first at the ordinary temperature and then after gentle warming to 40° to 50°; or, the solution can be effected in a beaker, provided with mechanical stirring apparatus, in the cold. Copper is at first precipitated, but eventually goes into solution with the formation of an inky cuproso-cupric compound; the whole operation need not take more than an hour. The residue contains carbon, silicon, phosphorus, and sulphur, together with a little iron. It is filtered upon ignited asbestos, washed with a small quantity of the solvent, then with boiling water, and dried in the steam-bath.

*Combustion of the Residue in Oxygen.* To oxidise the residue in oxygen, the asbestos filter containing the carbonaceous precipitate is placed in a boat and pushed into a heated combustion tube charged with copper oxide. A glass tube enables the progress of the combustion to be followed, but porcelain tubes are much more generally used, as higher temperatures can then be employed. The issuing gases are passed through tubes containing calcium chloride, anhydrous cuprous chloride, or anhydrous copper sulphate, before entering the absorption

<sup>1</sup> Cf. *Stahl u. Eisen*, 1887, 7, 13; 1891, 11, 50.

vessel. By placing a layer of potassium bichromate and a silver spiral behind the oxide of copper, any traces of sulphur and of chlorine are effectively retained. A detailed description of the most modern apparatus and procedure for this method of carbon estimation is given by Blair.<sup>1</sup>

*Oxidation of the Residue with Chromic Acid.* As an alternative to the above method the carbonaceous residue may be oxidised by chromic acid according to Ullgren's method. The residue is filtered off into a tube 75 mm. long and 15 mm. wide, upon a pad of ignited asbestos. The filter is brought bodily into a conical flask, having a tubulure and a ground-in dropping funnel, but no condenser. The apparatus is then connected up, tested to make sure that it is air-tight, a litre of purified air drawn through, the absorption tubes attached, and the oxidising solution introduced. This consists of one volume of chromic acid solution (3 : 10) to five volumes of sulphuric acid of sp. gr. 1.83, 40 c.c. of the mixture being added for each 1.0 g. of iron. The contents of the flask are heated to boiling very slowly, over a period of one to one and a half hours, and boiled for a short time; 3 to 4 litres of purified air are then drawn through and the absorption tubes subsequently detached and weighed.

*Gas-volumetric Methods for the Determination of the evolved Carbon Dioxide.* The carbon dioxide produced by wet combustion may be determined gas-volumetrically instead of by absorption and weighing. Various methods and apparatus for this purpose have been described by Wiborgh,<sup>2</sup> Vogel,<sup>3</sup> Lunge and Marchlewski,<sup>4</sup> Reinhardt,<sup>5</sup> Hempel,<sup>6</sup> and others.

The apparatus devised by Lunge (Fig. 13) consists of a 200 c.c. flask A having a dropping funnel, also of 200 c.c. capacity, fused into the side. Into the neck is ground the inner tube of a short Liebig's condenser *d*, which, at the upper end communicates, through the ground-glass joint *e*, with the capillary tube *f* and the gas-volumeter BCD. At *a* and *c* the grinding must be so perfect that air-tight connections are secured by merely moistening with water; at *e* a ground-glass joint is not strictly necessary, and can be replaced by a rubber connection, provided care be taken that the glass surfaces are in contact. The metal is first treated with copper sulphate as above (p. 52). The apparatus is then connected up and a partial vacuum obtained by raising and lowering D six times; the stopcock *h* is then closed. The proper quantity of oxidising mixture, made up according

<sup>1</sup> *The Chemical Analysis of Iron*, p. 134.

<sup>2</sup> *Stahl u. Eisen*, 1887, 7, 465; *J. Soc. Chem. Ind.*, 1887, 6, 748; 1890, 9, 768.

<sup>3</sup> *Stahl u. Eisen*, 1891, 11, 486.

<sup>4</sup> *Z. angew. Chem.*, 1891, 4, 412; *J. Iron and Steel Inst.*, 1894, ii., 484.

<sup>5</sup> *Stahl u. Eisen*, 1892, 12, 648; *J. Iron and Steel Inst.*, 1892, ii., 511; 1893, i., 403.

<sup>6</sup> *Ibid.*, 1895, i., 503.

to the table on p. 52, is then run in through *t* and *a*, the tap *a* closed, and the tap *h* opened so as to connect A with B, the levelling tube lowered, and the process of wet combustion carried out as previously described. Owing to the action of the condenser, no actual moisture gets into B, but the entering gases are saturated with aqueous vapour. After boiling, hydrogen peroxide is introduced into A (*cf.* p. 53), and the remaining air displaced by pouring in hot water until the capillary is full of liquid up to the stopcock *h*, which is then closed. The volume of air and carbon dioxide in B is measured, transferred once or twice into the Orsat pipette E, which is charged with concentrated potassium hydroxide solution, and the residual gas measured. Should the original volume of the gases be less than 140 c.c., purified air must be drawn in through *n* and *m* up to this volume, in order that readings may be obtained on the stem of the gas-burette. The use of the reduction tube C is explained fully in Vol. I., pp. 138 *et seq.*

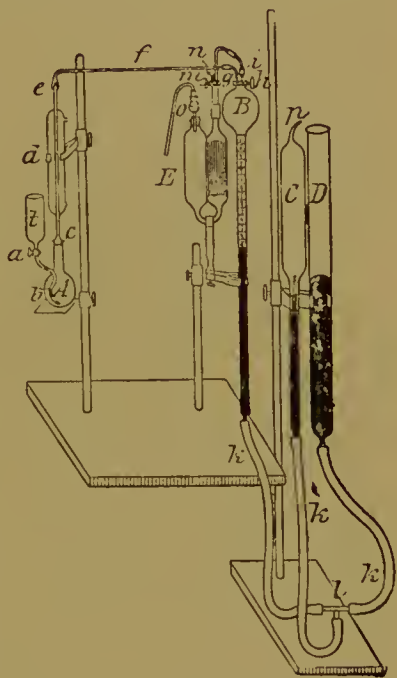


FIG. 13.

Each cubic centimetre of carbon dioxide at 0° and 760 mm. corresponds to 0.539 mg. of carbon.

4. *Preliminary separation of Carbon followed by Colorimetric estimation.* The colorimetric method of estimating carbon proposed by Peipers,<sup>1</sup> is similar in principle to the jeweller's touchstone assay, and is useful for rough tests. The metal is rubbed on a plate of unglazed porcelain until a streak of approximately standard depth of colour is produced. A graded series of streaks is made in the same way with steels of known carbon content (Fig. 14). The porcelain plates are

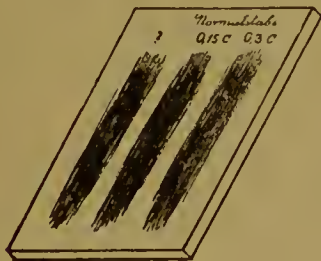


FIG. 14.

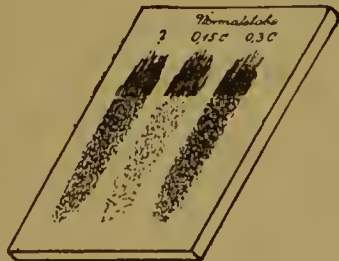


FIG. 15.

then dipped in a 12 per cent. solution of ammonium copper chloride. When both the iron and copper have been dissolved away, the plates

<sup>1</sup> *Stahl u. Eisen*, 1895, 15, 999; *J. Iron and Steel Inst.*, 1895, ii., 587.



are dipped in water and the residual stains (Fig. 15) of carbon are compared. In this way the carbon content of the test-piece is placed between two limits. In the figures, the streak of the test-piece is shown on the extreme left, by the side of streaks of standards containing 0.15 per cent. and 0.30 per cent. of carbon respectively.

Some practice is required for making comparable streaks with metals of varying hardness. The method is distinguished from Eggertz's colorimetric assay (p. 57) in indicating total carbon, no matter in what form the carbon may be present.

5. *Preliminary Separation of Carbon by Volatilisation of the Iron and Combustion of the Residue.* For this purpose the metal is heated either in a current of chlorine (Wöhler)<sup>1</sup> or of hydrochloric acid gas (Deville). It is an unpleasant and lengthy method, but is the only one which can be applied to refractory ferro-chromes and ferro-silicons.

The apparatus required consists of a 1500 c.c. flask for generating the chlorine, or preferably a cylinder of compressed chlorine; a wash-bottle containing water; a second wash-bottle containing concentrated sulphuric acid; a U-tube charged with glassy phosphoric acid; a combustion furnace with a tube at least 16 mm. wide bent at right angles at the further end and dipping into a beaker of sulphuric acid.

The chlorine is generated from 280 g. of salt, 190 g. of pyrolusite, and 350 c.c. of dilute sulphuric acid (1 : 2). From 0.5 to 1.0 g. of metal is spread out as thinly as possible in a porcelain boat and introduced into the combustion tube. Chlorine is then passed through until the air is displaced, when the burners of the furnace are gradually lighted, one by one, and the tube finally heated to redness. A certain amount of chromic and manganous chlorides always remains in the boat.<sup>2</sup> The former, being insoluble in water, necessitates a further ignition of the boat in a tube through which hydrogen is passed, whereby it is reduced to soluble chromous chloride. Finally, the contents of the boat are washed into a beaker of cold water, filtered upon asbestos, and oxidised either in the dry or wet way, as described above.

Neumann<sup>3</sup> has described a method for the combustion of the residue in a specially constructed platinum crucible, and also a method for the direct combustion of the carbon by heating in an electric oven, in a current of oxygen, at 1000°.

**Graphite and Temper-Carbon.**—These forms of carbon are both characterised by being resistant to acids, and there is no known method of determining them separately. Temper-carbon is comparatively rare, and occurs chiefly in white pig iron, after prolonged heating to redness. The method of estimation described by Ledebur<sup>4</sup> is as follows:—

<sup>1</sup> *Chem. News*, 1867, 16, 67.

<sup>2</sup> Cf. Hampe, *Chem. Zeit.*, 1890, 14, 1777.

<sup>3</sup> *Stahl u. Eisen*, 1908, 28, 128; Cf. also Mars, *ibid.*, 1909, 29, 1155.

<sup>4</sup> *J. Iron and Steel Inst.*, 1891, i., 364; 1893, ii., 53; 1899, i., 368.



One gram of highly graphitic iron, 2 to 3 g. of light grey pig or annealed white pig iron are taken for the determination. The metal is dissolved in a conical flask with 25 c.c. of nitric acid of sp. gr. 1.2 for each gram of substance. During the first violent action the flask is cooled in water. It is then digested on the sand-bath for two hours, just short of boiling, with frequent agitation. The liquid is diluted somewhat, filtered upon ignited asbestos, and the black residue washed with cold water till free from iron; the filter and its contents are then either oxidised by chromic acid or dried and heated in a current of oxygen, and the graphitic carbon weighed as carbon dioxide.

**Combined Carbon.**—As mentioned above, carbide-carbon can be determined separately, whereas hardening-carbon can only be estimated by difference. The following colorimetric method of Eggertz indicates, strictly speaking, carbide-carbon only. But when iron is allowed to cool down from white heat under ordinary smelting or foundry conditions—that is, when it is neither chilled in water or oil, nor annealed in a non-conducting covering—the carbide- and hardening-carbons in it are present in a fairly constant ratio. Hence, by the choice of proper standards, Eggertz's method, which is a purely comparative one, may serve to show the whole of the combined carbon.

The method is applicable to all kinds of malleable iron and steel, but not to nickel or chrome steels, because the greenish or yellowish tints of the solution interfere. It is based on the fact that when iron is dissolved in nitric acid, the combined carbon also goes into solution, with the result that the liquid is coloured more or less deeply brown. Ferric chloride, if present, affects the colour; the nitric acid used must, therefore be free from chlorine. Dilution to at least 8 c.c. for each 0.1 g. of the sample eliminates the influence of the colour of the ferric nitrate. Phosphorus, sulphur, copper, and silicon have but little effect upon the accuracy of the determination. Tungsten is converted into the insoluble oxide and is filtered off, together with the graphitic carbon; the weak tinctorial effects of manganese and vanadium disappear on dilution.

To carry out the estimation, the solution of the metal under examination is diluted until it shows the same tint as a similarly prepared solution of a standard metal, in which the carbon has been accurately determined by one of the foregoing gravimetric methods.

The procedure laid down by Eggertz<sup>1</sup> is as follows:—0.1 g. of a standard steel containing say 0.8 per cent. of carbon, and the same quantity of the metal under assay (or 0.05 g. in the case of white pig iron) are placed in separate test tubes, 15 mm. wide and 12 cm. long, and treated with small quantities of nitric acid of sp. gr. 1.2 so long as there is any effervescence. The balance of acid is then added in the following proportions: for 0.25 per cent. of carbon, 2.5 c.c.; for 0.3 per

<sup>1</sup> *Chem. News*, 1881, 44, 173.

cent., 3 c.c.; for 0.5 per cent., 3.5 c.c.; and for 0.8 per cent., 4 c.c.; white pig requires 7 c.c. A slight excess of acid is harmless, but a deficiency should be avoided. When the carbon content is unknown, 2.5 c.c. of acid are taken to begin with, and more is added in accordance with the colour and the amount of carbide precipitate produced. The test tubes are loosely stoppered and placed, through a perforated lid, in a water-bath, which is kept at the boiling point. After three-quarters of an hour all the carbon is obtained in solution and no more gas is evolved. Sometimes a red deposit, resembling a sublimate, of basic ferric nitrate forms on the sides of the vessel; this is loosened by shaking up, and filtered off if necessary; or else recourse may be had to the older method of digesting for one and a half to two hours at 80°, when the deposit is not formed. Spüller<sup>1</sup> hastens solution by placing the tubes in a paraffin bath heated to 135°, when five minutes suffice. Auchy<sup>2</sup> weighs out 1.0 g. of metal, in order to secure a fairer sample, and, after dissolving in 20 c.c. of acid, makes up to 25 c.c. and uses 5 c.c. of the solution. Whatever procedure be adopted, standard conditions must always be observed.

The test tubes, after heating, are removed from the water-bath and allowed to cool, being carefully protected from light, which has a marked bleaching action on the colour. The contents are then transferred to colorimeter tubes of 30 c.c. capacity, graduated in twentieths of a c.c. The standard solution is so diluted with water that each c.c. corresponds to say 0.1 per cent. of carbon. Then water is added to the solution of the sample until both solutions show the same tint, care being taken to secure thorough mixing. Some workers prefer to make the colorimetric comparison under exclusion of laterally impinging light. For this purpose the graduated tubes are placed in a blackened box of pyramidal shape, 26 mm. broad at the illuminated end and 12 cm. broad at the observing end, with two perforations in the upper side to receive the tubes.

By this method, the carbon content can only be determined in intervals of  $\frac{1}{10}$  per cent. In modern iron and steel practice a higher degree of delicacy is necessary, and the colorimetric assay must be modified accordingly. Either a number of standard steels of progressive carbon contents may be employed, or the standard solution prepared as above may be diluted down to one-half, one-fifth, one-tenth, and one-twentieth of its strength; the former method is, on the whole, to be preferred.

Solutions of white pig iron tend to become turbid through separation of a humus-like substance; hence it is desirable to make the assay as rapidly as possible. Chilled steel cannot be assayed directly by Eggertz's

<sup>1</sup> *Stahl u. Eisen*, 1899, 19, 825; *J. Iron and Steel Inst.*, 1899, ii., 482.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1903, 25, 999.

method; by heating the sample to a temperature slightly above the critical temperature, however, the hardening-carbon is converted into carbide-carbon, and the method can then be employed.

In Britton's modification<sup>1</sup> of Eggertz's method, a large number of normal solutions—viz., fifteen, representing carbon contents of from 0.02 to 0.3 per cent., is prepared; the test solution is made up to a definite volume and compared with the nearest of the standards. As the latter are very unstable, Britton proposed to use alcoholic solutions of burnt sugar or of coffee of standardised tints; but even these do not keep indefinitely. Eggertz then suggested standards prepared on the following lines from metallic salts, which can be depended on not to change their tints. Ferric chloride is dissolved in water containing 1.5 per cent. of hydrochloric acid of sp. gr. 1.15; similarly, cobalt chloride and cupric chloride are dissolved in water containing 0.5 per cent. of hydrochloric acid; in all cases the dilution is such that each c.c. contains 0.01 g. of metal. A mixture of 8 c.c. of ferric chloride solution, 6 c.c. of cobalt chloride solution, and 3 c.c. of cupric chloride solution, together with 5 c.c. of water containing 0.5 per cent. of hydrochloric acid, yields a liquid having the same colour as a solution of iron in nitric acid corresponding to 0.1 per cent. of carbon per c.c. This liquid can be further diluted with acidified water to any desired standard tint; the dilution is very nearly proportional to the content of carbon.

In the colorimetric method proposed by Stead,<sup>2</sup> the comparison is not made directly on solutions of iron in nitric acid, but on the filtrates obtained after precipitating the iron as hydroxide. One gram each of the standard and of the test metal are dissolved in nitric acid of sp. gr. 1.2 at 90° to 100°; 30 c.c. of hot water and 13 c.c. of sodium hydroxide solution of sp. gr. 1.27 are added, the liquids thoroughly shaken, made up to 60 c.c., allowed to settle for ten minutes, and filtered. A 50 mm. column of the standard solution is then poured into one graduated tube and the height of the test solution in a similar tube adjusted so that the tints appear equally intense when the tubes are illuminated from below. The percentages of carbon are then inversely proportional to the lengths of the columns of liquid. It is claimed that the accuracy of the method is not affected by the presence of hydrochloric acid or of hardening-carbon.

In order to determine *carbide-carbon* by itself, iron carbide must first be separated from the accompanying metallic iron and hardening-carbon. C. G. F. Müller<sup>3</sup> found that iron carbide is insoluble in cold, very dilute acid, but is decomposed by strong acid or at higher temperatures.

<sup>1</sup> *Chem. News*, 1872, 26, 139.

<sup>2</sup> *J. Iron and Steel Inst.*, 1883, p. 213; *Chem. News*, 1883, 47, 285.

<sup>3</sup> *Stahl u. Eisen*, 1888, 8, 292; *J. Iron and Steel Inst.*, 1888, ii., 295; 1895, i., 495.



The method of estimation accordingly consists in dissolving 1 to 3 g. of finely comminuted material in a conical flask, through which hydrogen, carbon dioxide, or coal gas is passed, by means of dilute sulphuric acid (30 c.c. of 1 : 10 acid for each gram of metal) at the ordinary temperature. With frequent shaking, the time required for solution is from two to three days. Hardening-carbon escapes in the form of hydrocarbons. The residue is filtered upon asbestos, washed with cold water, and oxidised either with oxygen or with chromic acid. Graphitic carbon, if present, is determined separately and subtracted.

The colorimetric estimation of the carbon in steels containing small quantities of nickel and chromium can only be carried out by comparing the solutions of the samples with standard steels containing approximately the same amount of these metals (Lambert).

**Manganese.**—All the methods described for determining manganese in iron ores are applicable to metallic iron (*cf.* pp. 15 to 17); many of them, indeed, were originally worked out for iron and subsequently modified so as to be suitable for the analysis of ores. There are several methods, however, chiefly volumetric, which are better adapted for the estimation of manganese in iron than in ores.

Cast iron and ordinary steels usually contain less than 1.0 per cent. of manganese; iron for puddling or for the Bessemer process contains from 2 to 4 per cent., spiegel from 5 to 20 per cent., and ferromanganese up to 90 per cent. As a rule, 1 g. is a sufficient quantity to weigh out for analysis; in the case of highly manganiferous irons, 0.5 g., or even less, is enough. Malleable iron always contains a few tenths per cent. of manganese, so that 1 g. may be taken; welding iron, however, is often so poor in manganese that from 2 to 3 g. may be required.

Hydrochloric acid is used for dissolving the metal; if there is a considerable residue, as in the case of grey pig, it may be rendered soluble by fusion with alkali. Whenever manganese is determined gravimetrically, as by any of the methods used for ores, the silicon must be rendered insoluble by evaporation to dryness, and may be filtered off or not, as occasion demands.

The following are among the more important volumetric methods:—

1. *The Volhard-Wolff Permanganate Method* (*cf.* p. 34). The sample is weighed into a covered porcelain dish or into a conical flask about 75 mm. wide at the base, dissolved in 15 c.c. of nitric acid of sp. gr. 1.2, and evaporated to dryness. The mass is taken up with 20 c.c. of hydrochloric acid, boiled with 3 g. of potassium chlorate until free from chlorine, diluted, filtered into a litre conical flask, and the residue washed with water containing hydrochloric acid. The liquid is then treated with zinc oxide and the determination completed as described on p. 35.

When there are many estimations to be carried out, a saving of



time may be effected by using the modified method proposed by v. Reis.<sup>1</sup> One gram of iron is dissolved in 25 c.c. of a mixture consisting of 275 volumes of water, 125 of nitric acid of sp. gr. 1.4, and 100 of concentrated sulphuric acid. The liquid is boiled down over a free flame until fumes of sulphuric acid are disengaged, allowed to cool, diluted with 100 c.c. of water and 10 c.c. of the acid mixture, warmed to dissolve the salts, and transferred to a litre conical flask. The contained carbon is then oxidised by adding 3 g. of barium peroxide and 5 c.c. of concentrated nitric acid, and the excess of peroxide destroyed by boiling. The liquid is diluted with 300 to 400 c.c. of hot water, treated with zinc oxide, and titrated with permanganate; v. Reis prefers to add excess of permanganate and titrate back with a solution of manganous sulphate equivalent to the standard permanganate.

2. *The Hampe and Ukena Chlorate Method.*<sup>2</sup> This method takes advantage of the fact that manganese peroxide is precipitated from manganese salts on boiling with nitric acid and potassium chlorate. The precipitate is never free from iron, and cannot, therefore, be estimated gravimetrically. Iron does not interfere in the volumetric estimation, but cobalt, lead, and bismuth, if present, are partially precipitated and affect the results. In this case the precipitate is simply dissolved by means of nitric and oxalic acids and reprecipitated with chlorate. Copper, nickel, tin, and phosphorus have no injurious effect. The main requirements are:—1, That the solution be very concentrated; 2, that sulphuric acid, if present in more than moderate quantity, must be removed by adding barium nitrate; and 3, that hydrochloric acid must be absent.

For the determination, the metal is dissolved in 70 c.c. of nitric acid of sp. gr. 1.2, in a 500 c.c. flask, the hot, clear solution allowed to cool down, 11 g. of potassium chlorate crystals added through a wide-neck funnel, and the liquid gently boiled for from twenty-five to forty minutes down to a volume of 30 to 40 c.c. In the case of ferromanganese the concentration must be carried to the furthest possible limit. By this time all chlorine should have been boiled away; this is essential to the success of the precipitation. If the liquid be boiled too violently, the precipitate is apt to become slimy and difficultly soluble.

Grey pig iron is treated with 50 c.c. of acid in a beaker and evaporated to half the volume. The liquid is cautiously diluted with hot water without disturbing the sediment, filtered into a flask, evaporated, and treated with chlorate as above.

The concentrated liquid is next very carefully diluted with water. As the precipitate of manganese peroxide has a great tendency to pass

<sup>1</sup> *Z. angew. Chem.*, 1892, 5, 604, 672; *J. Soc. Chem. Ind.*, 1893, 12, 378.

<sup>2</sup> *J. Iron and Steel Inst.*, 1885, p. 652.

through filter paper, care must be taken to disturb it as little as possible. The supernatant liquid is first filtered through a double filter, and, when all the liquid has passed through, then the precipitate collected; washing is continued until the filtrate no longer reacts with starch and potassium iodide. The filtrate is tested for manganese by boiling with chlorate, when there should be no further precipitation; or, preferably, a portion is boiled with nitric acid and lead or bismuth peroxide and filtered through asbestos, when the presence of manganese is indicated by the formation of permanganic acid.

Ten c.c. of standard ferrous ammonium sulphate solution are then run into the flask from a burette, whereby any adherent manganese peroxide is dissolved. The filter paper is pierced, its contents washed into the flask with a little water and more standard solution dropped on to the filter, which soon becomes quite white when it is again washed. A further quantity of standard solution is run into the flask, so that all the manganese is dissolved, the total volume read off, dilute sulphuric acid (1 : 3) added to the solution, and the excess of ferrous ammonium sulphate titrated back with standard permanganate.

The permanganate solution must be standardised under the conditions of the assay. For this purpose 0.1 g. of chemically pure potassium permanganate is dissolved in 60 c.c. of nitric acid of sp. gr. 1.2 with the aid of a few crystals of oxalic acid, and precipitated as above. The strength of the standards should be such that 1 c.c. corresponds to about 1 to 5 mg. of manganese. Oxalic acid may be used as the reducing solution in place of ferrous ammonium sulphate.

In applying this method to iron ores, 5 g. are dissolved in hydrochloric acid, the residue fused, the extract added to the original solution, and the whole made up to 500 c.c. Two separate portions, each of 100 c.c., are evaporated to dryness, taken up with nitric acid, filtered, and precipitated as above. Ores rich in manganese and containing little silica may be dissolved directly in nitric acid with the addition of oxalic acid, a slight excess of which is of no consequence.

3. *G. v. Knorre's Persulphate Method*.<sup>1</sup> On boiling manganese sulphate in acid solution with ammonium persulphate, the manganese is precipitated as hydrated peroxide, since manganese persulphate is stable only in the cold. The reaction is as follows:—



The precipitate is too impure to be weighed, and must be estimated volumetrically by means of standard ferrous ammonium sulphate and potassium permanganate solutions. These solutions should be standardised from mixtures of manganese and iron salts containing these metals approximately in the proportion of the test.

<sup>1</sup> *Z. angew. Chem.*, 1901, **14**, 1149; 1903, **16**, 905.

To carry out the estimation, the metal is dissolved in a beaker in 50 to 60 c.c. of warm dilute sulphuric acid (1 : 10) and filtered into a 500 c.c. conical flask. Highly siliceous ferromanganese leaves a manganiferous residue, which is evaporated in a platinum crucible with sulphuric and hydrofluoric acids, dissolved in a little water, and added to the original solution. Ammonium persulphate solution (60 g. per litre) is then added to the liquid, in the proportion of 150 c.c. or 250 c.c., according as less or more than 1 g. of metal was weighed out, and the volume diluted to from 250 to 300 c.c. After boiling for fifteen minutes, the liquid is allowed to settle, and filtered, with the usual precautions, upon a dense filter of 8 cm. diameter, or on a double filter. The precipitate is then treated as described under method No. 2.

Lüdert<sup>1</sup> has modified this method as follows:—From 2 to 4 g. of the sample are dissolved in from 25 to 50 c.c. of nitric acid of sp. gr. 1.2, the solution heated to boiling and diluted with 400 c.c. of water without filtering; 40 c.c. of sulphuric acid and 50 c.c. of ammonium persulphate are then added. After boiling for half an hour to decompose the manganese persulphate and the excess of ammonium persulphate, the solution is cooled by placing the flask in cold water, and 5 c.c. of a titrated solution of hydrogen peroxide added. When the whole of the manganese peroxide has gone into solution, the excess of hydrogen peroxide is titrated back with permanganate. It is necessary to standardise the hydrogen peroxide solution with the permanganate each day on account of its instability.

In presence of tungsten the method is modified as follows<sup>2</sup>:—From 2 to 10 g. of tungsten steel are dissolved in dilute sulphuric acid in absence of air, the solution gradually heated to boiling, and boiled for a few minutes. On cooling, the metallic tungsten is filtered off as rapidly as possible, as it oxidises fairly readily in the air and would then go into solution, washed two or three times with water, and the manganese estimated in the filtrate as described. The precipitate of hydrated manganese peroxide must be dissolved by ferrous sulphate, not by hydrogen peroxide; the latter acts upon any traces of tungsten that may be present in the solution, and would accordingly lead to too high results for the manganese.

4. *Persulphate Oxidation Method.* A method much in vogue in steel works' laboratories in which a large number of manganese determinations have to be made daily, consists in dissolving 0.2 g. of the sample in 10 c.c. of nitric acid of sp. gr. 1.2 in a boiling-tube. A number of the tubes are then placed into boiling water until solution is complete and all nitrous oxide fumes expelled. Fifteen c.c. of silver nitrate solution (1.33 g. per litre) are then added to the contents of each tube, together with 1 g. of slightly moist persulphate of

<sup>1</sup> *Z. angew. Chem.*, 1904, 17, 422.

<sup>2</sup> G. v. Knorre, *Stahl u. Eisen*, 1907, 27, 380.



ammonium crystals. The tubes are replaced in the water-bath, which is kept boiling until the manganese is oxidised to permanganate and the action of the persulphate is no longer apparent. A small additional quantity of persulphate is added to the contents of each tube, and the whole of the tubes are then cooled in cold water. The permanganate formed is estimated by sodium arsenite solution, which is run in from a carefully graduated burette, the solution being titrated in a porcelain dish; the reaction is completed when the colour of the permanganate is discharged and a pale greenish coloration formed. The arsenite solution is made up from a stock solution containing 5 g. of arsenious acid and 15 g. of sodium bicarbonate per litre; 80 c.c. of this solution are diluted to 1000 c.c. for the titration. The value of the arsenite solution is obtained by titrating a solution of 0.2 g. of steel of known manganese content (Lambert).<sup>1</sup>

5. *Other Volumetric Methods.* The method of Meinecke<sup>2</sup> (p. 37), which depends on the titration of an excess of potassium permanganate employed to precipitate manganese peroxide, is modified as follows for the estimation of manganese in metallic iron. Solution is effected by means of a mixture of three volumes of sulphuric acid (1 : 4) and one volume of nitric acid of sp. gr. 1.10; the carbonaceous matter is oxidised by boiling with 0.5 c.c. of chromic acid (1 : 1), the excess of the latter removed by adding barium chloride, and the iron and chromium then precipitated with zinc oxide. Zinc chloride is added to the permanganate for the precipitation, instead of zinc sulphate. The volume displaced by the precipitate has to be taken into account, which can be done by weighing out 0.9947 g. of metal in place of 1 g. It is well to subject the manganiferous liquid to partial filtration before pouring it into the permanganate.

Schneider<sup>3</sup> oxidises the manganese to permanganic acid and titrates back with hydrogen peroxide (*cf.* Vol. I., p. 109). The decomposition takes place in accordance with the equation:—



Two grams of steel or pig iron are dissolved in 200 c.c. of nitric acid of sp. gr. 1.2 and heated to boiling with a considerable excess of lead or bismuth peroxide. The liquid is immediately cooled down, filtered through asbestos, and titrated with hydrogen peroxide diluted with two or three volumes of water, the strength of which has been determined by means of standard permanganate. Lead peroxide is apt to be manganiferous, and must be tested by decomposing a sample

<sup>1</sup> *Cf.* also P. Smith, *Chem. News*, 1904, 90, 237; Rubricius, *Stahl u. Eisen*, 1905, 25, 890; 1910, 30, 957.

<sup>2</sup> *Stahl u. Eisen*, 1886, 6, 444.

<sup>3</sup> *Dingl. polyt. J.*, 1888, 269, 224; *J. Iron and Steel Inst.*, 1892, ii., 512.



with hot sulphuric acid, cooling, diluting, and warming with a fresh portion of the peroxide; manganese, if present, will then produce a more or less pink solution. Steels containing chromium cannot be assayed by this method. Metals containing more than 2 per cent. of manganese are preferably assayed by the Volhard-Wolff process.

6. *Colorimetric Method.* When a permanganic solution has been prepared as described under method No. 1, the manganese can be estimated by comparing the tint with a solution of potassium permanganate of known strength. This standard is made up by dissolving 0.072 g. of permanganate in 500 c.c. of water (1 c.c. = 0.05 mg. Mn); the solution does not keep well, especially if exposed to light. According to Ledebur, to carry out the determination, 0.2 g. of metal are dissolved in 15 to 20 c.c. of nitric acid of sp. gr. 1.2 in a 100 c.c. flask, the solution boiled to expel nitrous fumes, allowed to cool, and made up to the mark. Ten c.c. are then heated to boiling with 2 c.c. of nitric acid in a small beaker, a pinch of lead peroxide added, and the liquid boiled up for two minutes. After settling, it is filtered through ignited asbestos into an Eggertz colorimeter tube (p. 57). One to four c.c. of permanganate solution are introduced into a second tube, and diluted until the two liquids have the same depth of tint. Then, if  $x$  be the required percentage of manganese,

$$b : c = \frac{a}{4} : x,$$

where  $a$  is the volume of standard permanganate, and  $b$  and  $c$  the volumes, respectively, of standard and test solutions in the colorimeter tubes.

**Nickel.**—Minute quantities of nickel occur in various raw and refined irons. Nickel steels usually contain several per cent.

1. *Nickel Oxide Method.* For the estimation, 2 to 5 g. of iron or steel, or 1 to 5 g. in the case of nickel steel, are dissolved in hydrochloric acid with the aid of nitric acid or potassium chlorate, evaporated to dryness, taken up with hot dilute hydrochloric acid, and filtered. Ammonium chloride and an excess of ammonia are added to the filtrate, the precipitate filtered off and redissolved, the precipitation being then repeated twice as above. The united filtrates are evaporated to a small bulk, and, if necessary, the ammonium salts are removed by taking to dryness and igniting. Sulphuretted hydrogen is then passed into the warm acid solution to precipitate copper and antimony, which are filtered off, the filtrate made just ammoniacal, and treated with ammonium sulphide. The combined precipitates of manganese and nickel sulphides are treated on the filter with cold dilute hydrochloric acid (1:6). The nickel sulphide, which remains undissolved, is thoroughly washed and ignited to NiO.

2. *Nickel Sulphide Method.* Ledebur removes the bulk of iron by means of the ether-extraction method (*cf.* p. 9). The extracted solution of chlorides is then heated to expel ether, diluted, and treated with sulphuretted hydrogen to precipitate copper. After boiling off the sulphuretted hydrogen from the filtrate, it is oxidised with nitric acid, and the residual iron removed as basic ferric acetate; the nickel is then precipitated from the boiling acetic solution by sulphuretted hydrogen.

3. *Dimethylglyoxime Method.* A more recent method, due to O. Brunck,<sup>1</sup> which is both rapid and accurate, consists in the precipitation of nickel by means of dimethylglyoxime,  $\text{CH}_3\text{.CNOH.CNOH.CH}_3$ , whereby it can be separated from iron, chromium, zinc, manganese, and cobalt. Dimethylglyoxime is a white, crystalline powder, insoluble in water, but soluble in warm alcohol. A 1 per cent. alcoholic solution is used for the precipitation; this produces a bright red precipitate of the nickel compound, which can be readily washed, and which, when dried at  $110^\circ$  to  $120^\circ$ , has the composition  $\text{C}_8\text{H}_{14}\text{N}_4\text{O}_4\text{Ni}$ , and contains 20.31 per cent. Ni. A slight excess of ammonia is necessary to secure complete precipitation.

Iron, if present, is either completely oxidised to the ferric state, and the solution then treated with tartaric acid to prevent its precipitation by ammonia, or it is reduced by sulphur dioxide to the ferrous condition, and the nickel precipitated in dilute acetic acid solution in presence of sodium acetate; the former procedure is adopted in presence of chromium. Small quantities of manganese, copper, or vanadium do not influence the results; if considerable quantities of manganese be present, the precipitation must be effected in acetic acid solution.

To carry out the method, 0.5 to 0.6 g. of nickel steel are dissolved in 10 c.c. of hydrochloric acid, which should not be too concentrated, and oxidised with nitric acid. If any silica separates, it is dissolved by the addition of hydrofluoric acid. From 2 to 3 g. of tartaric acid are then added, the whole diluted to 300 c.c., and a small excess of ammonia added to make sure that no precipitation occurs; the solution is then just acidified with hydrochloric acid and heated to boiling. The precipitation of the nickel is next effected by the addition of 20 c.c. of the dimethylglyoxime solution, ammonia being subsequently added, drop by drop, to ensure complete precipitation. The precipitate can be filtered at once; but in the case of specially accurate determinations, it is preferable to allow it to stand for twenty-four hours. The precipitate is collected either in a porcelain or platinum Gooch crucible, washed six to eight times with water, and dried at  $100^\circ$  to  $120^\circ$  till constant.

Iwanicki<sup>2</sup> avoids the use of a Gooch crucible by collecting the precipitate on a dried filter paper, using a similarly dried filter paper as

<sup>1</sup> *Z. angew. Chem.*, 1907, **20**, 834, 1844; *J. Soc. Chem. Ind.*, 1907, **26**, 643, 1217.

<sup>2</sup> *Stahl u. Eisen*, 1908, **28**, 1547.

a tare. Wdowiszewski<sup>1</sup> converts the precipitate to nickel oxide by careful ignition; to avoid the sublimation of the glyoxime compound, the precipitate is rolled up in the moist filter paper, and then wrapped in a second filter paper before ignition.

4. *Dicyanodiamidine Method.* In this method, introduced by H. Grossmann and Schück,<sup>2</sup> nickel is precipitated by dicyanodiamidine sulphate. The precipitation is effected in an ammoniacal solution of a nickel salt in presence of an excess of potassium or sodium hydroxide; the precipitate is pale yellow and crystalline, and has the composition when air-dry,  $\text{Ni}(\text{C}_2\text{H}_5\text{N}_4\text{O})_2 \cdot 2\text{H}_2\text{O}$ .

For the determination, from 0.5 to 2.0 g. of the sample, according to the content of the nickel, are dissolved in aqua regia, the solution evaporated down to 15 c.c., any separated silica filtered off, and Rochelle salt added to the filtrate to prevent the precipitation of iron; from 15 to 20 g. are added in a 50 per cent. solution for every 1 g. of iron. If much manganese be present, hydrazine sulphate is added to prevent its being precipitated with the nickel. On the addition of the Rochelle salt a precipitate of acid potassium tartrate separates, which is coloured yellow by the enclosed mother-liquor; this is dissolved by ammonia, and an excess of sodium hydroxide added (50 c.c. of a 20 per cent. solution). The solution turns bright green, and should be perfectly clear. The nickel is then precipitated with 1 to 1.5 g. of dicyanodiamidine sulphate (preferably in 10 per cent. solution), the precipitate allowed to stand for several hours, filtered off on a Gooch crucible, washed four to five times with 6 per cent. ammonia, dried at  $120^\circ$  to  $130^\circ$  and weighed. The anhydrous compound contains 22.5 per cent. of nickel.

5. *Potassium Cyanide Volumetric Method.* The following rapid method of determining the approximate percentage of nickel in a nickel steel is employed in many laboratories (Lambert).<sup>3</sup>

One gram of the sample is dissolved to a clear solution in 20 c.c. of nitric acid (1 : 1), the nitrous fumes boiled off, 100 c.c. of distilled water added, and the solution allowed to cool. Fifteen c.c. of ammonium-citrate solution (225 g. citric acid, 450 c.c. strong ammonia, and 150 c.c. water) are added, the whole neutralised with strong ammonia, and, when quite neutral, not more than 1 c.c. of ammonia added in excess. A crystal of potassium iodide is then stirred in and the solution titrated with a solution of potassium cyanide containing silver nitrate (48.5 g. potassium cyanide, 0.5 g. silver nitrate, and 2000 c.c. water). The opalescence produced by the first additions of the cyanide solution is

<sup>1</sup> *Stahl u. Eisen*, 1908, 28, 960; 1909, 29, 358; cf. also P. Bogoluboff, *Stahl u. Eisen*, 1910, 30, 458; *J. Soc. Chem. Ind.*, 1910, 29, 493.

<sup>2</sup> *Chem. Zeit.*, 1907, 31, 535, 911; *Stahl u. Eisen*, 1909, 29, 143; cf. also Prettner, *Chem. Zeit.*, 1909, 36, 396, 411; *J. Soc. Chem. Ind.*, 1909, 28, 525.

<sup>3</sup> Cf. G. T. Dougherty, *Chem. News*, 1907, 95, 261, 268; and C. M. Johnson, *J. Amer. Chem. Soc.*, 1907, 29, 1201.



cleared up by further addition of cyanide until the solution remains crystal-clear for at least three minutes. The cyanide solution is standardised against a known nickel steel or against 30 mg. of pure electrolytic nickel, which represents steel containing about 3.0 per cent. of nickel. The strength of the cyanide solution is so adjusted that approximately 30 c.c. are used for 30 mg. of nickel.

This method is equally applicable for steels in sulphuric acid solution.

6. *Electrolytic Method.* Neumann<sup>1</sup> has worked out the following electrolytic method for the estimation of nickel in nickel steel. From 2.5 to 5 g. of the metal are dissolved in dilute sulphuric acid, the solution oxidised with hydrogen peroxide and ammonium sulphate, and an excess of ammonia added. The liquid is boiled up, thoroughly shaken, allowed to cool, and made up to 500 c.c. The precipitated iron is then filtered off and 100 c.c. of the clear solution withdrawn by a pipette, or separated by filtration through a dry filter paper, for electrolysis. So much ammonium sulphate is added that the total quantity reaches 10 g., and in addition, 30 to 40 c.c. of ammonia and 20 to 60 c.c. of water. An electromotive force of  $3\frac{1}{2}$  to 4 volts, with a current density of 1 to 2 ampères per square decimetre, is used for the electrolysis, the liquid being warmed up to 50° to 60°. The time required is about two hours. The accuracy of the method is not affected by the presence of silicon, carbon, or chromium, provided that the last be not present as chromic acid. Manganese is, at most, deposited in traces with the nickel.

**Aluminium.**—Aluminium may be present up to 10 per cent. as a constituent of ferro-aluminium, or in very small quantity in cast iron, to which it has been added as a deoxidiser. The analysis of ferro-aluminium is perfectly straightforward. It dissolves readily in acids, and the further procedure is the same as for argillaceous iron ores (*cf.* p. 9). The determination of small quantities of aluminium in presence of much iron is, on the other hand, somewhat difficult by the ordinary methods of analysis; it is, however, much facilitated by the use of the ether-extraction method (p. 9) for the removal of the bulk of the iron.

According to Carnot,<sup>2</sup> aluminium is precipitated completely as phosphate from dilute acetic acid solution on boiling, even in presence of a large excess of iron, provided the latter be in the ferrous condition. To carry out the estimation, 10 g. of metal are dissolved in hydrochloric acid and neutralised, first with ammonia and finally with sodium carbonate. Sodium thiosulphate is added until the solution is colourless, then 2 to 3 c.c. of a saturated sodium phosphate solution and 20 c.c.

<sup>1</sup> *Stahl u. Eisen*, 1898, 18, 910; *J. Soc. Chem. Ind.*, 1898, 17, 1074.

<sup>2</sup> *Comptes rend.*, 1890, 111, 914; *Chem. News*, 1881, 44, 85; 1891, 63, 10, 85, 172.



of sodium acetate solution, and the liquid boiled for three-quarters of an hour; the smell of sulphur dioxide should be no longer noticeable at the end of this time. The precipitate is washed with warm water, dissolved in hydrochloric acid, the solution evaporated to dryness, the silica filtered off, and the aluminium again precipitated as above, and weighed as  $\text{AlPO}_4$ , which contains 22.18 per cent. Al.

Modifications of this method have been described by Stead<sup>1</sup> and by Borsig.<sup>2</sup>

Ziegler<sup>3</sup> first eliminates silica, reduces the ferric chloride with sodium hypophosphite, precipitates the alumina with zinc oxide, repeats the precipitation after filtration and dissolving, again dissolves and precipitates twice successively with ammonia; a final purification is effected, after ignition, by fusion with alkali carbonates.

Schöneis<sup>4</sup> dissolves the metal in nitric acid, evaporates to dryness, and fuses the residue with aluminium-free potassium hydroxide; the filtered extract is acidified and precipitated with ammonia. The alumina thus obtained may contain more or less silica, according to the nature of the metal; this is removed by evaporating with hydrofluoric acid.

Schneider<sup>5</sup> has pointed out that all the above methods involve the use of reagents which may introduce more aluminium than is actually present in the metal. He, therefore, regards it as essential that the methods employed should involve the use of such reagents only as are easily obtained pure and easily tested, and from this standpoint has suggested the following method, in which the reagents are restricted to ammonia, tartaric acid, and ammonium sulphide.

Twelve grams of iron are dissolved in 150 c.c. of nitric acid of sp. gr. 1.2, and 12 g. of tartaric acid and 400 c.c. of ammonia (1 : 1) added. A bulky precipitate is formed, which redissolves to a very dark, clear solution on heating to 100°. The liquid is transferred to a two-litre flask, diluted with hot water, treated with 100 c.c. of ammonia (1 : 1) freshly saturated with sulphuretted hydrogen, the whole well shaken, allowed to cool, and made up to the mark. After the precipitate has settled, it is filtered through a dry filter paper, and 1500 c.c. of the filtrate (=9 g. of metal) evaporated to dryness with nitric acid, and the residue gently ignited and treated with hydrofluoric and sulphuric acids to expel the silica. The residue thus obtained contains the oxides of vanadium and titanium, together with alumina; it is fused with alkali carbonate, the melt dissolved in sulphuric acid, and the alumina precipitated as usual.

<sup>1</sup> *J. Soc. Chem. Ind.*, 1889, 8, 966.

<sup>2</sup> *Stahl u. Eisen*, 1894, 14, 6.

<sup>3</sup> *Dingl. polyt. J.*, 1890, 275, 526; *J. Iron and Steel Inst.*, 1891, i., 440.

<sup>4</sup> *Stahl u. Eisen*, 1892, 12, 527; *J. Iron and Steel Inst.*, 1892, ii., 518.

<sup>5</sup> *Oesterr. Zeitschrift*, 40, 471.

The ether-extraction process for the preliminary removal of the iron (*cf.* p. 9) offers such marked advantages for the determination of aluminium that it is likely to supersede the methods described above. From 5 to 10 g. of iron are dissolved in hydrochloric acid and evaporated to dryness. The residue is lixiviated with dilute hydrochloric acid, the silica filtered off, the filtrate evaporated with addition of nitric acid to about 12 c.c., and extracted with ether. The aluminium is then precipitated as phosphate from the residual solution, as described on p. 11.

**Chromium.**—Chrome steels are soluble in sulphuric acid, hydrochloric acid, or aqua regia. Ferro-chrome, however, is resistant towards acid, and has to be treated by fusion.

Ziegler<sup>1</sup> fuses 0.5 g. of ferro-chrome in a silver crucible with 6 g. of sodium hydroxide and 3 g. of nitre. The charge is heated up very gradually, so as to reach complete fusion in half an hour. The melt is taken up with water, saturated with carbonic acid, evaporated to dryness, lixiviated, filtered, and the residue washed with water containing sodium carbonate. By this procedure an efficient separation of iron and chromium is usually attained; it is desirable, however, to test the ferric residue, both for unattacked metal and for chromium.

Namias<sup>2</sup> fuses 1 g. of ferro-chrome with 8 to 10 g. of acid potassium sulphate; after fusing for one hour, 2 to 3 g. more of acid sulphate are added and melted up. The mass is dissolved in dilute hydrochloric acid, the silica filtered off, the filtrate nearly neutralised with sodium hydroxide, and precipitated by means of 2 g. of magnesia suspended in water. The precipitate is filtered, washed, ignited, and fused with a mixture of sodium carbonate and nitrate; all the chromium is thus ultimately obtained as sodium chromate.

Spüller and Brenner<sup>3</sup> mix 0.35 g. of finely ground ferro-chrome with 2 g. of dry powdered sodium hydroxide, with a silver spatula in a silver crucible, and cover the mixture with a layer of 4 g. of sodium peroxide. The mixture is rapidly heated up to incipient fusion; the burner is then withdrawn during the violent reaction which occurs. After the first reaction is over, the crucible is ignited for ten minutes, 5 g. of sodium peroxide carefully stirred in, the fusion continued for thirty minutes, a further 5 g. of peroxide added, and the mass again ignited for twenty minutes; the oxidation should then be complete. Finally, another 5 g. of peroxide are incorporated, in order to facilitate the lixiviation, and the crucible immediately allowed to cool. The further procedure is the same as in the case of chromiferous ores (*cf.* p. 17).

In the case of chrome steel, 2 g. are dissolved in 20 c.c. of strong hydrochloric acid and the solution evaporated to dryness with 10 c.c. of

<sup>1</sup> *Dingl. polyt. J.*, 1889, 274, 513; *Chem. News*, 1892, 66, 295.

<sup>2</sup> *Stahl u. Eisen*, 1890, 10, 977; *J. Iron and Steel Inst.*, 1890, ii., 853.

<sup>3</sup> *Chem. Zeit.*, 1897, 21, 3; *Stahl u. Eisen*, 1897, 17, 101.

sulphuric acid (1 : 1). The residue is heated to expel excess of acid, transferred to a silver crucible, and then treated like ferro-chrome.

When it is desired to separate iron from chromium without having recourse to fusion, one of the following methods may be adopted.

According to Galbraith,<sup>1</sup> 5 g. of steel are dissolved, without access of air, in 25 c.c. of hydrochloric acid of sp. gr. 1.12 and 200 c.c. of water. It is important to keep all the iron in the ferrous condition, as ferric chloride is precipitated by barium carbonate, whilst ferrous chloride is not. The solution is accordingly effected in a flask with an attached tube dipping into distilled water, as shown in Fig. 4, p. 33, or in a Contat-Göckel bulb (*cf.* Vol. I., p. 106). After complete solution, the liquid is diluted to about 400 c.c. and barium carbonate cautiously added, so as to be present in slight excess. The flask is then stoppered, allowed to stand for twenty-four hours, and shaken at intervals. The precipitated chromium hydroxide is filtered off, washed with cold water, dissolved in hydrochloric acid, and reprecipitated with ammonia. Sometimes the chromic oxide thus obtained is pure enough to weigh, but it is safer to fuse it with 3 g. of sodium carbonate and 0.5 g. of nitre, lixivate, filter, evaporate to dryness with hydrochloric acid and alcohol, and precipitate the clear solution of chromic chloride with ammonia.

Reinhardt<sup>2</sup> dissolves 10 g. of metal in 100 c.c. of hydrochloric acid of sp. gr. 1.19, oxidises the solution with potassium chlorate, evaporates to 50 c.c., filters, heats to boiling, and gradually adds 10 to 20 c.c. of a solution of sodium hypophosphite (200 g. dissolved in 400 c.c. of cold water and filtered after standing for some days). An excess of zinc oxide cream is then added to the reduced solution. The precipitate of chromic hydroxide is filtered off, washed, dissolved in hot hydrochloric acid, reprecipitated with zinc oxide after again reducing with a little sodium hypophosphite, redissolved and reprecipitated twice successively with ammonia, to remove the zinc. The thoroughly washed precipitate, together with the original residue insoluble in acid, is finally fused with an oxidising mixture (*e.g.*, 8 g. of a mixture of four parts fused sodium chloride, one part sodium carbonate, and one part potassium chlorate), and a solution of alkali chromate thus obtained.

In dealing with pig iron containing very little chromium, Donath<sup>3</sup> proceeds as follows:—Three grams of metal are dissolved in hydrochloric acid (1 : 1) and the solution heated to boiling. Meanwhile a solution of sodium carbonate is heated up in a porcelain dish. Both solutions are tinged a full red by the addition of potassium permanganate. The iron solution is then slowly run into the sodium carbonate; the iron and manganese are precipitated, whilst the chromium remains

<sup>1</sup> *Dingl. polyt. J.*, 1887, 266, 399.

<sup>2</sup> *Stahl u. Eisen*, 1889, 9, 404; *J. Iron and Steel Inst.*, 1889, ii., 480.

<sup>3</sup> *Stahl u. Eisen*, 1894, 14, 446; *J. Iron and Steel Inst.*, 1894, ii., 493.



in solution as sodium chromate. The excess of permanganate is decomposed by alcohol, and the filtrate is then ready for the determination of the chromium.

Stead<sup>1</sup> separates chromium from iron by precipitation as phosphate from a neutral solution in presence of sodium thiosulphate and acetate as in the method previously described for aluminium, fuses the precipitate with magnesia and sodium hydroxide, and so obtains sodium chromate.

Whenever the chromiferous metal is soluble in acids, it is always advantageous to remove the bulk of the iron by extraction with ether (*cf.* p. 9).

The gravimetric determination of chromium in sodium chromate solutions is carried out as described under the analysis of ores (p. 17).

To determine chromium volumetrically, a solution of 14 g. of ferrous ammonium sulphate in 1 litre of water, standardised against decinormal potassium permanganate, is used. The chromate solution is diluted, acidified with sulphuric acid, and reduced with the ferrous solution, the excess of which is titrated back with permanganate. The iron value of the solution, divided by  $52.12 : 167.64 = 0.3109$ , gives the value for chromium, since 3 g.-mol. of ferrous ammonium sulphate are oxidised by one equivalent of chromium. When the chromium is very small in amount, it is preferable, according to Zulkowski,<sup>2</sup> to titrate with potassium iodide and standard sodium thiosulphate, a check determination being carried out simultaneously with a known quantity of a standard potassium bichromate solution. The solution of the chromate corresponding to 1 g. of the sample is treated with 10 c.c. of potassium iodide solution (1 : 10), hydrochloric acid of sp. gr. 1.12 added, and the liberated iodine titrated with sodium thiosulphate after standing for fifteen minutes in the dark. Twenty c.c. of a potassium bichromate solution, containing 0.9918 g.  $K_2Cr_2O_7$  per litre = 0.00695 g. Cr per 20 c.c., are similarly titrated. The sodium thiosulphate solution contains 4.966 g.  $Na_2S_2O_3 \cdot 5H_2O$  per litre.

Schneider<sup>3</sup> dissolves 2 g. of chrome steel in dilute sulphuric acid, oxidises with 5 c.c. of strong nitric acid, boils off the nitrous fumes, adds 5 g. of lead peroxide, boils again for a quarter of an hour, and filters. The filtrate is rendered ammoniacal, and boiled for a short time till the permanganate that has been formed is decomposed. Sulphuric acid is then added to dissolve the precipitate and the solution (filtered if necessary) titrated as above, after dilution to 1 litre. Should the solution, after the precipitation of iron, be so poor in chromium (less than 0.1 per cent.) as not to appear yellow, it is separated by partial filtration, the filtrate acidified with sulphuric acid, and titrated.

<sup>1</sup> *J. Iron and Steel Inst.*, 1893, i., 160.

<sup>2</sup> *Chem. Zeit.*, 1897, 21, 3; *Stahl u. Eisen*, 1897, 17, 101.

<sup>3</sup> *Oesterr. Zeitschrift*, 40, 235; *J. Iron and Steel Inst.*, 1892, ii., 515.



The following volumetric methods for the estimation of chromium in iron and steel are due to A. W. Gregory and J. MacCallum.<sup>1</sup> Two grams of the metal are dissolved in as little nitric acid as possible and silver nitrate and ammonium persulphate added; after boiling, ammonium chloride is added in sufficient quantity to precipitate nearly all of the silver, the solution diluted to a definite volume, and filtered through asbestos. A quantity of the filtrate equal to half the original volume of the solution is taken, excess of standard ferrous sulphate solution added, to reduce the chromate which has been formed, and the excess of ferrous sulphate determined by titration with standard potassium bichromate solution.

Chromium can also be determined by means of sodium bismuthate. Two grams of the steel are dissolved in nitric acid, and about 3 g. of bismuthate added in small quantities at a time; the solution is boiled till all the manganese is precipitated as dioxide, enough very dilute hydrochloric acid added to dissolve the manganese dioxide, and then excess of silver nitrate. The solution is boiled, made up to a definite volume, filtered through asbestos, and an aliquot portion titrated with ferrous sulphate and bichromate as above.

A colorimetric method for the estimation of chromium has been described by Hillebrand.<sup>2</sup>

**Tungsten.**—Tungsten steel and ferro-tungsten are soluble in acids, whereas metallic tungsten is almost insoluble. All methods of assay are based upon the separation of tungstic acid, which is purified and weighed as tungsten trioxide.

In the case of tungsten steel, 1 to 2 g. are dissolved in dilute nitric acid and the solution evaporated down with sulphuric acid, as in the determination of silica by Drown's method (p. 45). The insoluble residue obtained on lixiviation is treated with hydrofluoric acid to expel silica, and ignited, but not over the blast. The trioxide is always contaminated with iron. According to Auchy,<sup>3</sup> the amount of this impurity is practically constant, viz., from 0.02 to 0.03 per cent. for steels containing less than 1 per cent. of tungsten, and from 0.03 to 0.04 per cent. for those which contain a higher proportion; it cannot be removed by washing with hydrochloric acid. In order to obtain perfectly pure trioxide, the impure substance is converted into sodium tungstate by fusion with sodium carbonate, the melt lixiviated, the solution evaporated to dryness with nitric acid, and extracted with water; the trioxide thus left behind is filtered off, washed with dilute ammonium nitrate solution, dissolved in ammonia, evaporated to dryness in a platinum vessel, and ignited and weighed.

<sup>1</sup> *J. Chem. Soc.*, 1907, **91**, 1846. Cf. also G. v. Knorre, *Stahl. u. Eisen*, 1907, **27**, 1251, and Phillips. *Ibid.*, 1907, **27**, 1164.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1898, **20**, 454; *Chem. News*, 1898, **78**, 227.

<sup>3</sup> *J. Amer. Chem. Soc.*, 1899, **21**, 239; *J. Chem. Soc.*, 1899, **76**, 524.

Herting<sup>1</sup> determines tungstic acid volumetrically by titration with sodium hydroxide. The precipitated acid, still contaminated with silica and iron, is washed on the filter with dilute nitric acid and then with 5 or 10 per cent. potassium nitrate until the filtrate is neutral. It is then rinsed into a flask, boiled up with 200 c.c. of water, and titrated whilst hot with  $N/1$  sodium hydroxide, phenolphthalein being employed as indicator. One c.c. of sodium hydroxide solution neutralises 0.116 g. of  $WO_3$ , equivalent to 0.092 g. of tungsten.

A method for the estimation of tungsten by precipitation with benzidine sulphate has been worked out by G. v. Knorre.<sup>2</sup>

Ferro-tungsten dissolves readily in aqua regia, but since some of the metal always escapes attack through being coated with tungstic acid, it is better to proceed by fusion from the start. Alkali carbonate and nitre, or sodium hydroxide and peroxide, or acid potassium sulphate, or a mixture of three parts of fusion mixture with two parts of anhydrous borax,<sup>3</sup> may be used.

Metallic tungsten is converted into the trioxide by roasting, either alone (Preusser<sup>4</sup>) or with ammonium nitrate (Ziegler<sup>5</sup>). This is then further converted into sodium tungstate, either in the wet or dry way, and the clear solution evaporated with nitric acid, as above.

A method for dissolving ferro-tungsten, proposed by Namias,<sup>6</sup> consists in boiling the finely powdered alloy with concentrated sodium hydroxide or carbonate solution, to which bromine has been added.

**Molybdenum.**—This element, like tungsten, is met with in molybdenum steel, which contains up to 3 per cent., and in ferro-molybdenum, used in the manufacture of the steel. It may be determined by oxidising to molybdic acid, separating from iron, reducing to  $Mo_{12}O_{19}$ , and titrating with potassium permanganate.<sup>7</sup>

Convenient quantities for analysis are 1.5 g. of steel or 0.3 g. of ferro-molybdenum. The metal is dissolved in nitric acid, with or without addition of potassium chlorate, evaporated to dryness, redissolved in 20 c.c. of hydrochloric acid of sp. gr. 1.19, again evaporated to dryness, and taken up with 10 c.c. of hydrochloric acid. The solution is poured into 100 c.c. of 10 per cent. sodium hydroxide solution, contained in a 300 c.c. measuring flask, made up to the mark, and thoroughly shaken. It is then filtered through a dry filter paper into a capacious flask, and 200 c.c. of the clear filtrate treated with 80 c.c. of hot dilute sulphuric acid (1:4) and 10 g. of zinc, and the liquid warmed, without actually boiling, for twenty to twenty-five

<sup>1</sup> *Z. angew. Chem.*, 1901, 14, 165.      <sup>2</sup> *Stahl u. Eisen*, 1906, 26, 1491; 1908, 28, 986.

<sup>3</sup> Wdowiszewski, *Stahl u. Eisen*, 1895, 15, 675.

<sup>4</sup> *Z. anal. Chem.*, 1889, 29, 173; *Chem. News*, 1889, 60, 37.

<sup>5</sup> *Chem. Zeit.*, 1889, 13, 1060; *Chem. News*, 1889, 60, 272.

<sup>6</sup> *Stahl u. Eisen*, 1891, 11, 757; *J. Chem. Soc.*, 1892, 62, 539.

<sup>7</sup> Auchy, *J. Amer. Chem. Soc.*, 1902, 24, 273.

minutes, until the reduction is complete. It is then rapidly freed from zinc by filtration and titrated with  $N/10$  or  $N/20$  potassium permanganate. The iron value of the permanganate, multiplied by 0.606, gives the molybdenum.

**Vanadium.**—According to Blum, this element is present in minute quantities in most pig irons, ores, and slags. It also occurs as an ingredient of vanadium steel.

Ledebur<sup>1</sup> determines vanadium as follows:—Ten grams of pig, 2 to 5 g. of vanadium steel, or 0.3 g. of ferro-vanadium are dissolved in boiling dilute hydrochloric acid in a flask. After cooling, a slight excess of barium carbonate is added, and the flask filled up with water, corked, and allowed to stand for twenty-four hours. The precipitate is filtered off, washed, dried, mixed with 5 to 10 g. of a mixture of one part of nitre and fifteen parts of sodium carbonate, and fused in a platinum crucible. Should there be much graphite with the precipitate, it is well to burn it off before fusion. The melt is extracted with water, the filtrate acidified with hydrochloric acid, then made alkaline with ammonia, and a few cubic centimetres of yellow ammonium sulphide added; a slight excess of acetic acid is added to the red liquid thus obtained. On standing for at least twenty-four hours in a stoppered flask all the vanadium will be precipitated as the brown sulphide. This is filtered off, washed with water containing sulphuretted hydrogen, and ignited to  $V_2O_5$  in a platinum crucible. The oxide contains 56.14 per cent. of vanadium.

Chromium, if present, is precipitated together with vanadium by barium carbonate. In this case the extract, after fusion, is evaporated with hydrochloric acid and alcohol, the residue dissolved in dilute hydrochloric acid, and a few grams of potassium chlorate added to re-oxidise the vanadium. The liquid is then boiled with a drop or two of ammonium phosphate and the chromium precipitated by ammonia. The vanadium in the filtrate is precipitated as sulphide, as above.

For the determination of traces of vanadium in steel, 50 g. of the sample are dissolved in very dilute sulphuric acid (1:20); the acid is preferably mixed and cooled before using, and then allowed to act on the metal over night. The carbonaceous residue is collected on a filter, transferred while wet to a platinum dish, dried, ignited, and allowed to cool. The residue is thoroughly mixed with sodium carbonate and nitrate, fused for some minutes, extracted with boiling water, filtered, and dilute nitric acid added to the filtrate till just on the point of acidity; a few drops of sodium carbonate are then added, and the solution filtered from any small quantities of iron and manganese or silica that are precipitated. The filtrate is made slightly acid and the

<sup>1</sup> *Leitfaden f. Eisenhütten Laboratorien*, 6th edition, p. 119.

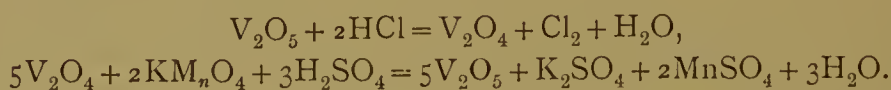


vanadium precipitated by mercurous nitrate, with the addition of mercuric oxide to ensure the neutrality of the solution.

The mercury precipitate obtained by boiling the solution contains, besides the vanadium, any tungsten, chromium, etc., that may have been present in the sample. The residue, after ignition of the mercury precipitate, is again fused with a little sodium carbonate and a little nitrate, and extracted with the minimum quantity of water. From this solution the vanadium is precipitated by saturating the solution with pure solid ammonium chloride. After a few hours, the separated vanadium is collected, washed with ammonium chloride solution, ignited, and weighed as the pentoxide,  $V_2O_5$  (Lambert).

The following volumetric method for the estimation of vanadium, due to E. Campagne,<sup>1</sup> is to be recommended in absence of chromium, or if only an inconsiderable quantity of this metal is present. From 2.5 to 5.0 g. of the sample, according to its content of vanadium, are dissolved in 60 c.c. of nitric acid of sp. gr. 1.18, and the solution evaporated to dryness in a porcelain dish; in the case of alloys rich in vanadium, 0.25 g. are taken and dissolved in 20 c.c. of acid. The residue is heated to decompose the nitrates, as in the estimation of phosphorus, dissolved in concentrated hydrochloric acid, the bulk of the iron removed by the ether-extraction process, the residual liquor evaporated twice successively almost to dryness, taken up with 50 c.c. of concentrated hydrochloric acid, and finally, again evaporated with 5 to 10 c.c. of concentrated sulphuric acid until acid fumes begin to be evolved. The solution is then allowed to cool, dissolved in 300 c.c. of water, warmed to about 60°, and titrated with dilute permanganate solution.

The initially formed vanadic acid is reduced by the hydrochloric acid, and the lower oxide then oxidised by the permanganate in accordance with the following equations:—



The iron-value of the permanganate solution, multiplied by 0.914, accordingly gives the value for vanadium; it is advisable to dilute the permanganate solution to five times its volume, on account of the small proportions of vanadium usually present, which gives 0.1828 as the conversion factor.

**Copper.**—The majority of the methods for determining copper in iron depend upon the separation of the copper as sulphide. When iron is dissolved to a ferrous salt in dilute sulphuric or hydrochloric acid, all or some of the copper remains undissolved. If, on the other hand, oxidation occurs during the solution, there is so much ferric salt formed, that direct treatment with sulphuretted hydrogen is out of the

<sup>1</sup> *Ber.*, 1903, 37, 3166.



question. A previous reduction of the iron is, therefore, necessary before precipitating the copper.

1. *Gravimetric Method.* At least 10 g. of metal are dissolved in 100 c.c. of hydrochloric acid of sp. gr. 1.19, with the aid of nitric acid, chlorate, or hydrogen peroxide, and evaporated to 50 c.c. The solution is reduced by means of 5 g. of sodium hypophosphite at boiling temperature; this salt does not react with sulphuretted hydrogen, so that an excess is of no consequence. Sulphuretted hydrogen is passed in to the warm solution<sup>1</sup> until saturated, and the precipitate, together with the original residue, filtered off and washed with hot water. It is then sprayed into a beaker, the filter ash added, the whole boiled with hydrochloric acid of sp. gr. 1.19 and 1 to 2 g. of potassium chlorate till completely dissolved, and the solution evaporated to dryness; the silica is filtered off and the copper precipitated as sulphide in the filtrate, and weighed, after ignition; or else the filtrate is freed from chlorides by evaporating with sulphuric acid and then subjected to electrolysis.

For reducing ferric chloride to the ferrous state, de Koninck<sup>2</sup> recommends acid sodium sulphite. According to v. Reis,<sup>3</sup> the precipitation of copper is conveniently effected by ammonium dithiocarbamate,  $\text{CS.NH}_2\text{.SNH}_4$ . The solution to be precipitated is diluted to 600 to 700 c.c., 10 c.c. of ammonium dithiocarbamate solution added to the stirred liquid, and the stirring continued for some time. On standing, copper sulphide settles out, and is filtered off without difficulty; it is washed with water containing 10 c.c. of ammonium dithiocarbamate solution and 20 c.c. of concentrated hydrochloric acid in the litre. The dithiocarbamate solution is prepared by shaking up 250 c.c. of concentrated ammonia, 250 c.c. of 95 per cent. alcohol, and 50 c.c. of carbon bisulphide; when the latter has gone into solution, the dark red liquid is diluted with four volumes of water.

Ledebur prefers to dissolve the metal with exclusion of air before precipitating the copper. He finds that the precipitate is hardly ever free from iron sulphide, and sometimes contains antimony sulphide; these admixtures have to be taken into account in the subsequent operations.

2. *Electrolytic Method.* Ten to twenty grams of iron are treated with 40 c.c. of dilute sulphuric acid, and a further 40 c.c. are added after the first reaction is completed. When nothing more goes into solution, the liquid is diluted to 200 c.c. and filtered. The residue is ignited in a porcelain crucible, dissolved in fuming nitric acid, evaporated with sulphuric acid until fumes are evolved, taken up with 20 c.c. of nitric acid of sp. gr. 1.2 and 20 c.c. of water, filtered, diluted to 120 c.c., and electrolysed with a current of 0.5 to 1.0 ampère per sq. dcm.

<sup>1</sup> Cf. Reinhart, *Stahl u. Eisen*, 1889, 9, 404.

<sup>2</sup> *Rev. Univ.*, 34, 235.

<sup>3</sup> *Stahl u. Eisen*, 1891, 11, 238; *J. Iron and Steel Inst.*, 1891, i., 441.

3. *Colorimetric Method.* This method, as described by Ziegler, has been modified by Perillon.<sup>1</sup> Solutions obtained by adding an excess of ammonia to copper nitrate are compared for depth of tint. The standard is made up by dissolving electrolytic copper in nitric acid and adding just enough ammonia to redissolve the precipitate. It is desirable to have two standards at hand, containing 2.0 and 0.2 mg. of copper per cubic centimetre, respectively.

The test solutions are prepared by precipitating the copper as sulphide and dissolving it in nitric acid. Colorimeter tubes, as employed for Eggertz's carbon assay, are used, and the test is diluted until it attains the tint of the standard (*cf.* p. 57). The method is very delicate, and is especially adapted to the estimation of very small amounts of copper.

**Arsenic and Antimony.**—Arsenic may be determined either by precipitation as arsenic sulphide and converting this into magnesium pyroarsenate, or by distillation as arsenic trichloride and subsequent precipitation with magnesia mixture. When iron is dissolved in hydrochloric acid, arseniuretted hydrogen is not evolved, unless the solution is made very acid. According to v. Ries,<sup>2</sup> arsenic may be relied upon not to escape as arseniuretted hydrogen when dilute sulphuric acid (1 : 5) is used.

1. *Sulphide Method.* Ten to fifty grams of metal are dissolved in hydrochloric acid of sp. gr. 1.19 and precipitated as for the determination of copper. The sulphides are dissolved, the silica and graphite filtered off, and the filtrate warmed with a slight excess of potassium hydroxide and sodium sulphide; the copper is thus precipitated, whilst arsenic remains in solution. The filtrate is acidified with hydrochloric acid and allowed to stand for a day. The precipitated arsenic sulphide is filtered, washed, and oxidised with hydrochloric acid and potassium chlorate. The solution is again filtered through a small filter paper, the filtrate concentrated to a few cubic centimetres, tartaric acid and an excess of ammonia added (which should produce no precipitate), and precipitated with magnesia mixture. At least twenty-four hours at the ordinary temperature are required to complete the precipitation of ammonium magnesium arsenate. The precipitate is treated exactly like the corresponding phosphorous compound, and is finally weighed as  $Mg_2As_2O_7$ . v. Reis<sup>3</sup> states that if the quantity of arsenic present is not too small, vigorous stirring and subsequent standing for fifteen minutes suffices to ensure the complete precipitation of the arsenic.

When, as very rarely happens, antimony is also present, it will pass into the filtrate from the above-mentioned magnesia precipitation. On acidifying, warming, and passing in sulphuretted hydrogen, antimony sulphide is precipitated, and can be converted into the oxide and weighed.

<sup>1</sup> *Dingl. polyt. J.*, 1892, 285, 142.

<sup>2</sup> *Stahl u. Eisen*, 1889, 9, 720.

<sup>3</sup> *Ibid.*, 1889, 9, 720.

2. *Distillation Method.* In this method, impure arsenic sulphide is precipitated as above, dissolved in hydrochloric acid with the addition of a little bromine, and then proceeded with as described on p. 21.

According to Stead,<sup>1</sup> the arsenic in the distillate may be determined directly by titration, instead of being converted into magnesium pyroarsenate. The distillate is rendered alkaline with ammonia, and then slightly acidified with hydrochloric acid. A small excess of sodium bicarbonate is added, together with some starch paste, and the solution titrated with standard iodine solution. The solutions required are:—

1. Arsenious acid: 0.66 g. of pure arsenic trioxide = 0.5 g. As, and 2 g. of sodium carbonate, are dissolved in 100 c.c. of boiling water. After cooling, 2 g. of sodium bicarbonate are added and the solution made up to a litre. One c.c. = 0.5 mg. As.

2. Iodine: 1.2692 g. of resublimed iodine and 2 g. of potassium iodide are made up to a litre. One c.c. = 1 c.c. of standard arsenious acid solution = 0.5 mg. As.

**Tin.**—Tin is quite an abnormal constituent of iron, but may be introduced by the use of tinplate scrap in the manufacture. It has sometimes to be determined in tinplate itself.

The usual method for the estimation of the tin is to dissolve the tinplate in hydrochloric acid, filter, and treat the filtrate with sodium carbonate or ammonia until a slight precipitate is formed; this is redissolved and the liquid saturated with sulphuretted hydrogen. After standing, the precipitate is collected, warmed with potassium sulphide solution to remove iron, lead, etc., and stannic sulphide precipitated from the filtrate by acetic acid; the precipitate is then evaporated in a porcelain crucible with nitric acid, ignited, and weighed as tin dioxide. One gram  $\text{SnO}_2$  = 0.7881 g. Sn.

According to Mastbaum,<sup>2</sup> when tinplate is boiled for a few minutes with 8 to 10 per cent. hydrochloric acid, all the tin is dissolved, with very little of the iron. He digests not less than 25 g. of tinplate snippets from two to four times successively with 50 c.c. of 10 per cent. hydrochloric acid, boiling for five minutes in a beaker each time, and pours the solutions into a graduated 250 c.c. flask. From the appearance of the metal, it can easily be judged when all the tin has been dissolved away. After making up to the mark, 50 c.c. of the solution are withdrawn with a pipette, ammonia added to incipient precipitation, and then 10 c.c. of yellow ammonium sulphide; the liquid is then well shaken and made up to 100 c.c. Fifty c.c. of the clear tin sulphide solution, = 2.5 g. of tinplate, are diluted, acidified with acetic acid, the precipitate allowed to settle, rinsed on to a filter with 10 per cent. ammonium acetate solution, the precipitate dried, and ignited to oxide,

<sup>1</sup> *J. Iron and Steel Inst.*, 1895, i., 110; *J. Soc. Chem. Ind.*, 1895, 14, 444.

<sup>2</sup> *Z. angew. Chem.*, 1897, 10, 330.



with repeated moistenings with ammonium carbonate. Or, if preferred, the sulphide solution may be taken directly to dryness and ignited.

The chlorine method of Lunge and Marmier<sup>1</sup> is considerably more rapid. Two to three grams of tinplate are cut into strips, introduced into a bulb-tube, and heated in a current of dry chlorine at a sufficiently low temperature so that the tin tetrachloride distils off, whilst the ferric chloride, if formed at all, does not volatilise. The further end of the bulb-tube is prolonged into the limb of a Peligot's U-tube charged with water, to which a second U-tube and a small conical flask are attached. Tin tetrachloride begins to distil off in the cold; as the reaction slackens, heat is gently applied, and after two to three hours the surface of the iron appears uniformly brown without white specks. Any tin chloride remaining in the U-tube is driven over by the aid of a small flame, and the chlorine is then displaced by a current of carbon dioxide. The end of the bulb-tube is cautiously washed out with dilute hydrochloric acid, taking care to avoid dissolving the ferric chloride; the receivers are similarly treated and the united liquids neutralised with ammonia until a slight precipitate is produced, which is redissolved by a drop or two of hydrochloric acid. The tin is then precipitated, either as metastannic acid by means of ammonium nitrate, or as sulphide.

A method based on the extraction of tin by fusion with sodium peroxide has been described by Augenot.<sup>2</sup> The flux is extracted with water, the ferric oxide filtered off, and the tin precipitated in the filtrate by acid, as hydroxide, and weighed as  $\text{SnO}_2$ .

**Sulphur.**—No kind of commercial iron is entirely free from sulphur, and its determination is a matter of great importance, as small quantities are sufficient to render refined irons and steels unfit for use.

The various methods proposed for the estimation of sulphur fall into three classes:—

1. Evolution of the sulphur as sulphuretted hydrogen and determination *via* metallic sulphides.

2. Evolution of the sulphur as sulphuretted hydrogen and conversion into barium sulphate.

3. Direct precipitation as barium sulphate.

1. *Evolution of the Sulphur as Sulphuretted Hydrogen and determination via Metallic Sulphides.* In these methods the sulphuretted hydrogen is absorbed without oxidation; the sulphides thus formed are determined either gravimetrically, volumetrically, or colorimetrically. The last method gives only approximate results, but the two former are very accurate.

*Gravimetric Method.* Silver, lead, copper, and cadmium salts have been proposed for the gravimetric absorption of sulphuretted hydrogen.

<sup>1</sup> *Z. angew. Chem.*, 1895, 8, 429.

<sup>2</sup> *Ibid.*, 1904, 17, 521.



Silver and copper salts, however, have been shown by Schulte<sup>1</sup> to be unsuitable, since other gases than sulphuretted hydrogen are evolved, which yield metallic silver with silver acetate and a yellow precipitate containing phosphorus with copper acetate. Schulte finds cadmium acetate, first proposed by Wiborgh, to be the best absorbent; it can be partially replaced by zinc acetate. The precipitated sulphide is converted into copper sulphide and ultimately weighed as cupric oxide. The absorbent is made up by dissolving 25 g. of cadmium acetate in a mixture of 250 c.c. of acetic acid and 250 c.c. of water on the water-bath, diluting to a litre, and filtering; or 5 g. of cadmium acetate and 20 g. of zinc acetate may be used as an economy. The solution for converting the cadmium sulphide into copper sulphide is made up by dissolving 120 g. of crystallised copper sulphate in 800 c.c. of water and 120 c.c. of concentrated sulphuric acid and diluting to one litre.

The apparatus which is best adapted for carrying out the determination is shown in Fig. 16. The use of a carbon dioxide generator and of a combustion furnace, formerly employed, is superfluous.

A is the decomposition flask, which is provided with a dropping funnel B, and an exit tube fitted with a three-way tap D; the wash-bottle E serves to collect the hydrochloric acid which distils off, and is connected to the absorption flask F.

Concentrated hydrochloric acid of sp. gr. 1.19 is used for the decomposition in preference to dilute acid, which was formerly employed, as it has been shown by Schindler,<sup>2</sup> by Reinhardt,<sup>3</sup> and by Schulte,<sup>4</sup> that with sufficient concentrated acid no organic sulphur is evolved, so that the use of a combustion furnace is unnecessary. It is necessary, however, to ensure that no hydrochloric acid is carried over from the wash-bottle into the absorption flask; as long as the concentration of the acid in the former does not exceed 12 per cent., there is no danger of this occurring.

To carry out the determination, 10 g. of the sample are placed in A, 160 c.c. of water in E, and 30 to 35 c.c. of the cadmium acetate solution in F. Fifty c.c. of hydrochloric acid are then run in from B, 25 c.c. being first added, and the remaining 25 c.c. after a short interval if the action is not too violent; a further 50 c.c. are subsequently added, similarly, making a total of 100 c.c. of acid. The decomposition is regulated so that three to four bubbles of gas are evolved per second; this is readily effected by employing a luminous flame provided with a regulator for the heating. The contents of the absorption flask must not be allowed to get hot during the decomposition. When the decomposition becomes slow, the flame is raised gradually until the solution approaches the boiling point, the tap of B then opened to prevent

<sup>1</sup> *Stahl u. Eisen*, 1896, 16, 867; *Chem. News*, 1897, 75, 47.

<sup>2</sup> *Z. angew. Chem.*, 1893, 6, 11.    <sup>3</sup> *Stahl u. Eisen*, 1906, 26, 799.    <sup>4</sup> *Ibid.*, 1906, 26, 985.

any sucking back from the wash-bottle, and the solution heated to boiling for eight to ten minutes. The decomposition flask is then detached, the burner moved to under the wash-bottle, the three-way tap D closed, and the contents of the wash-bottle heated to boiling for five minutes. The liquid in F is thereby warmed, and some 15 to 20 g. of water vapour, together with a very little hydrochloric acid, are condensed in it; the latter has no injurious effect. When the acetate solution is almost boiling the determination is complete, as all sulphuretted hydrogen will then have been driven out of the wash-

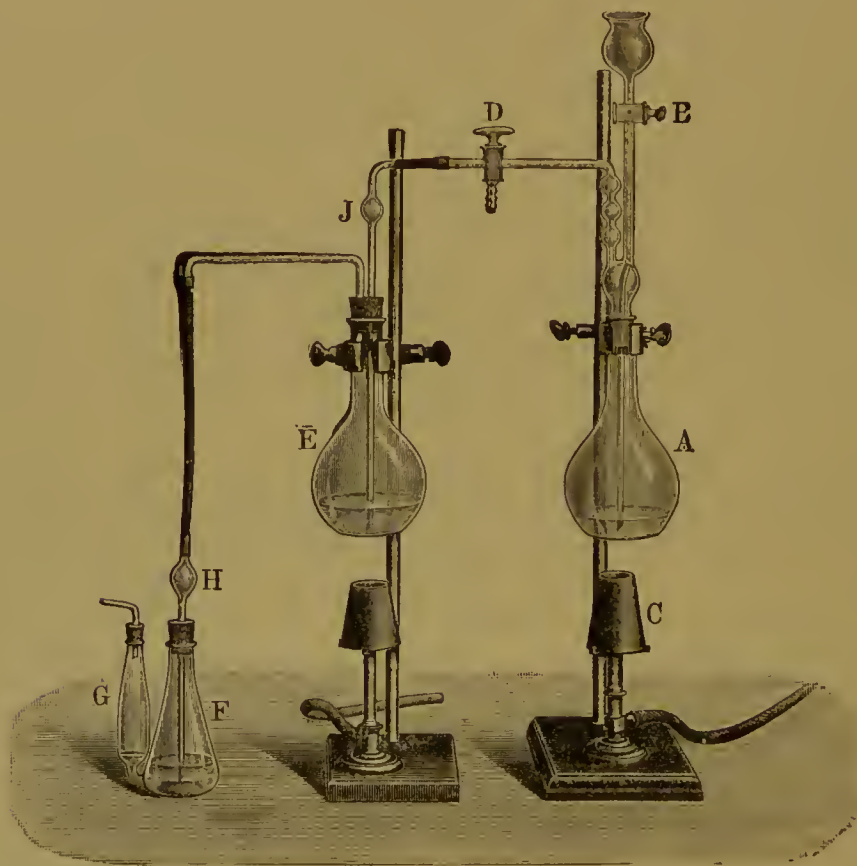


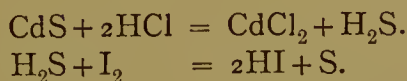
FIG. 16.

bottle. The residual solution in the decomposition flask can be used for the estimation of copper or of silicon. The contents of the absorption flask are then treated with 5 c.c. of the copper solution, prepared as described above, the precipitate collected on an ash-free filter paper, washed with slightly acidulated water, and ignited to cupric oxide in a platinum dish. The weight of  $\text{CuO} \times 0.403 = \text{S}$ .

*Volumetric Method.* In the volumetric method, as worked out by Reinhardt,<sup>1</sup> the cadmium sulphide is filtered off, treated with potassium iodide and hydrochloric acid, and the excess of iodine titrated back with

<sup>1</sup> *Stahl u. Eisen*, 1906, 26, 800.

sodium thiosulphate. The following equations represent the decompositions:—



The precipitate of cadmium sulphide is filtered, washed with ammonia (1 : 3), the filter paper and precipitate washed back into the original flask, 20 to 50 c.c. of standard iodine solution added, then 20 c.c. of hydrochloric acid (1 : 1) and 200 c.c. of water, and the solution titrated back with sodium thiosulphate, after the addition of starch solution.

*Colorimetric Method.* Wiborgh's<sup>1</sup> colorimetric method can lay no claim to accuracy, but is useful for rough and approximate tests. Sulphuretted hydrogen is evolved and made to pass through several layers of fabric impregnated with metallic salts, with which it gives a more or less pronounced colour. Discs, 80 mm. in diameter, of fine cotton sheeting, are soaked in a 5 per cent. aqueous solution of cadmium acetate, and are then laid on a clean linen cloth and allowed to dry. Cadmium acetate tends to give very uniform tints, and there is no danger of the sulphide being decomposed by the acid vapours evolved; but the acetate is somewhat unstable, and if the sulphur coloration turns out patchy, the test must be repeated. An escape of unabsorbed sulphuretted hydrogen need not be feared; when the sulphur content is very low, only the under side of the fabric is found to be coloured, and in no case does a second, superimposed disc show a coloration.

The apparatus used by Wiborgh (Fig. 17) consists of a wide-necked flask *a* with a rubber stopper holding a funnel *b*, and a cylindrical tube *c*. The latter is 58 mm. wide, and the fabric is held in position across its upper end by a rubber washer *d*,

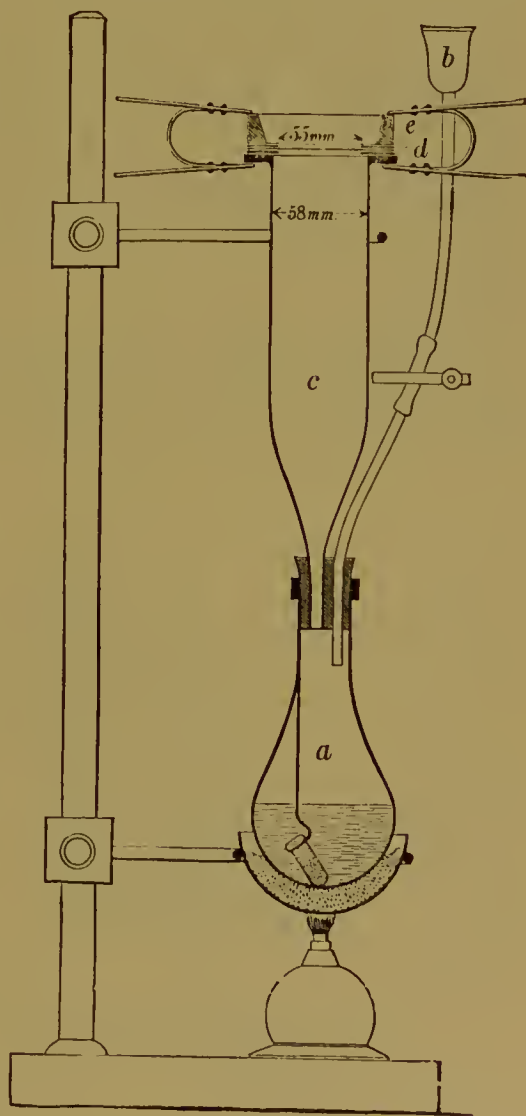


FIG. 17.

<sup>1</sup> *Stahl u. Eisen*, 1886, 6, 230; *Chem. News*, 1886, 54, 158.

and a wooden ring *c*, so that a circular area of 55 mm. is exposed. The flask is half-filled with distilled water, the metal introduced, and as much acid as may be required run in from *b*. At the outset the water in the flask is boiled up to expel the air, and the heating is continued until the test is completed. The depth of tint obtained on the fabric is estimated by comparison with a scale. It is essential that the lower, drawn-out end of *c* should be concentric with the body of the tube.

A scale of colorations is prepared by dissolving various weights of one and the same sample of iron, in which the sulphur has been accurately determined by other methods. Differences of tint are better observed when the total sulphur is low than when the proportion is considerable. This difficulty is met, however, by weighing out a greater or less quantity of the sample; thus, for a sulphur-content of 0.0025 per cent., 0.8 g. are taken, and for 2 per cent. 0.02 g. The scale prescribed by Wiborgh has seven degrees, obtained by treating 40, 80, 175, 267, 400, 629, and 800 mg. of iron respectively, containing 0.05 per cent. of sulphur. Identical results would be produced by 100 mg. of samples containing 0.02, 0.04, 0.08, 0.12, 0.20, 0.28, and 0.40 of sulphur respectively.

2. *Evolution of the Sulphur as Sulphuretted Hydrogen, and conversion into Barium Sulphate.* The apparatus employed in this method is shown in Fig. 18. Ten grams of the sample are introduced into the

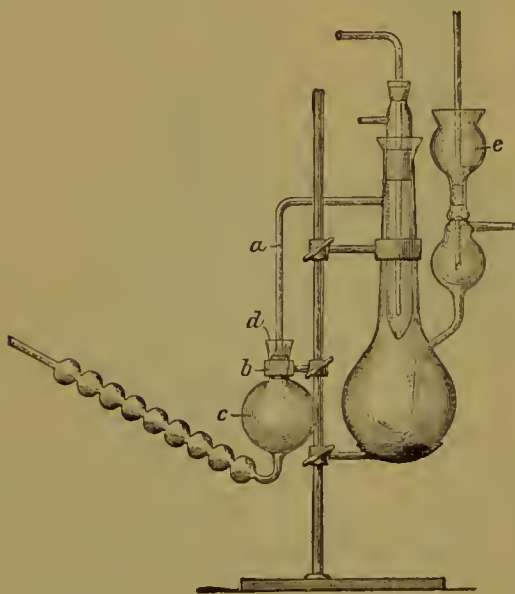


FIG. 18.

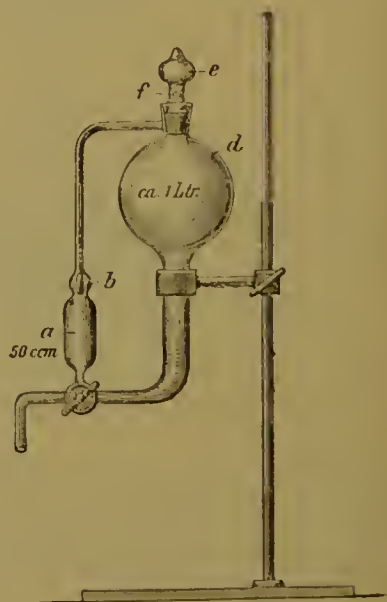


FIG. 19.

decomposition-flask, the contained air displaced by carbon dioxide, and then 50 c.c. of hydrochloric acid, saturated with bromine, placed in the absorption bulb.

The metal is dissolved by the addition of 100 c.c. of hydrochloric acid of sp. gr. 1.19, the solution boiled for five minutes, and a current



of carbon dioxide passed through for a further ten minutes. The contents of the absorption bulb are then washed out into a porcelain dish, 5 c.c. of sodium carbonate solution (1 : 10) added, the whole evaporated to dryness, taken up with 10 c.c. of hydrochloric acid (1 : 1) and water, and filtered. The solution is precipitated as usual with barium chloride, and the resulting barium sulphate ignited and weighed; any content of sulphur in the brom-hydrochloric acid must, of course, be determined by a blank experiment and deducted. The weight of  $\text{BaSO}_4 \times 13.744$  gives the per cent. of S.

The apparatus shown in Fig. 19 was devised by Corleis for measuring off the brom-hydrochloric acid.

3. *Direct precipitation as Barium Sulphate.* Krug,<sup>1</sup> Meinecke,<sup>2</sup> and Phillips<sup>3</sup> have pointed out independently that there are two sources of error in all methods of determining sulphur in iron and steel which depend on its liberation as sulphuretted hydrogen. On the one hand the whole of the sulphur is not evolved as sulphuretted hydrogen, dimethyl sulphide,  $(\text{CH}_3)_2\text{S}$ , being also formed, and on the other hand a portion remains behind in the decomposition in part as iron (and copper) sulphide. These sources of error have, however, been shown to be unimportant, if not illusory. To avoid them the only method is to completely oxidise the sulphur during solution to sulphuric acid and to precipitate it as barium sulphate. The results obtained by this method are, however, inaccurate, unless certain precautions are adopted, whilst the method is too lengthy to be used where numerous determinations are required.

The following form of this method has been worked out by Krug.<sup>4</sup> Five grams of the sample are dissolved in 50 c.c. of nitric acid of sp. gr. 1.4 in a 500 c.c. round-bottom flask. The solution is first warmed gently until the evolution of nitrous fumes has ceased, and then gradually heated to boiling; solution is complete in one to two hours. To prevent any volatilisation of sulphuric acid when the ferric nitrate is subsequently ignited, 0.25 g. of pure potassium nitrate are added, which retains the free sulphuric acid as potassium sulphate. The solution is evaporated to dryness, ignited, the residue dissolved in hydrochloric acid, evaporated till chlorine ceases to be evolved, the silica and insoluble matter filtered off, the filtrate concentrated, and the bulk of the iron removed by the ether-extraction method (p. 9). The sulphuric acid is then precipitated in the residual solution with barium chloride.

The results obtained by this method and by the bromine method of oxidation (No. 2) are concordant in the case of malleable iron and of steel, but they are less so in the case of cast iron.

Two opposing defects are, moreover, inherent in this method. On

<sup>1</sup> *Stahl u. Eisen*, 1905, 26, 887.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1896, 15, 218.

<sup>2</sup> *Z. angew. Chem.*, 1888, 1, 377.

<sup>4</sup> *Stahl u. Eisen*, 1905, 26, 887.

the one hand, barium sulphate is precipitated incompletely in presence of a large excess of acid; and on the other, precipitates from only moderately acid solutions tend to carry down more or less iron with them. By adopting certain precautions, these errors may be made to compensate each other to a considerable extent.

According to Platz,<sup>1</sup> 5 g. of pig iron are dissolved in nitric acid of sp. gr. 1.2, evaporated to dryness with hydrochloric acid, the residue dissolved in hydrochloric acid, the solution evaporated to syrupy consistency, diluted, filtered, and precipitated cold with barium chloride. After standing at the ordinary temperature for twelve hours, the barium sulphate is filtered off, washed with cold water, and burnt wet. Were the solution precipitated boiling, the barium chloride solution, which is apt to become basic during the evaporation, would precipitate a considerable quantity of the iron. In any case, a little iron, owing to adsorption by the filter, will be found in the ignited precipitate. The latter is, therefore, treated with a little hydrochloric acid and boiled with water and a drop of barium chloride, when pure, white barium sulphate, free from iron, is obtained.

Tamm<sup>2</sup> dissolves 5 g. of metal by boiling with 50 c.c. of water and 10 g. of potassium chlorate, and first adding 1 c.c. of hydrochloric acid to start the reaction; 5 c.c. of hydrochloric acid are then added, and further successive portions, each of 5 c.c., until there is no further evolution of chlorine and the metal is completely dissolved. The precipitation is then effected with barium chloride in the warm solution and the precipitate treated as above.

Schneider,<sup>3</sup> in criticising the above methods, holds that the iron contaminating the barium sulphate precipitate is present as ferric sulphate, which is liable to separate out of solution even in presence of much hydrochloric acid. When the precipitate is ignited, so much sulphuric acid as was combined with the iron escapes, and thus leads to low results. On further extracting the iron with acid, the error is increased in the same direction (*cf.* Vol. I., p. 275).

**Phosphorus.**—Phosphorus is determined in metallic iron in the same manner as in iron ores (p. 22). Two points have to be specially taken into consideration; the silicon must be entirely eliminated as silica, and the phosphorus must be fully oxidised to phosphoric acid.

The amount of metal to be weighed out depends on its nature; of iron for the basic process 0.5 g. is taken; of cast and puddling iron 1 to 2 g.; and of iron for the acid process 2 to 5 g.

1. *The Ignition Method.* The metal is dissolved, in a porcelain dish covered with a clock-glass, in 25 to 80 c.c. of nitric acid of sp. gr. 1.2, the solution evaporated to dryness, and the nitrates decomposed by

<sup>1</sup> *Stahl u. Eisen*, 1887, 7, 256; *J. Iron and Steel Inst.*, 1887, i., 471.

<sup>2</sup> *J. Iron and Steel Inst.*, 1887, ii., 369.

<sup>3</sup> *Oesterr. Zeitschrift*, 41, 365.

heating the residue on a wire gauze over the free flame. The silica is thus rendered insoluble, and the phosphorus is converted into phosphoric acid. The mass is warmed with 10 to 20 c.c. of concentrated hydrochloric acid and evaporated to syrupy consistency; 10 c.c. of nitric acid and (after a few minutes) hot water are added, the solution filtered, and the residue washed with dilute nitric acid. The filtrate, which should amount to about 100 c.c., is neutralised with ammonia, heated to nearly boiling with 1 g. of ammonium nitrate, and precipitated with 25 c.c. of molybdate reagent; fifteen minutes at  $80^{\circ}$  to  $90^{\circ}$  are allowed for complete precipitation. The phospho-molybdate is then filtered off, washed with nitric acid (1 : 1), dissolved in 10 c.c. of 50 per cent. citrate solution (*cf.* p. 23), washed with ammoniacal water, and precipitated with 2 c.c. of magnesia mixture, the further procedure being the same as in the analysis of ores. Should the solution be tinged green owing to the presence of reduced molybdic acid, this is oxidised by adding a few drops of hydrogen peroxide.

2. *The Oxidation Method* (v. Reis<sup>1</sup>). Oxidation by potassium permanganate is made use of, instead of ignition, in order to convert the phosphorous into phosphoric acid. The metal is dissolved in nitric acid and 25 c.c. of permanganate (10 g. to the litre) added, together with 8 to 10 g. of ammonium chloride, which effects the re-solution of precipitated manganese peroxide. The liquid is boiled until clear, evaporated to dryness, and proceeded with as in the ignition method.

Malleable iron and steel generally contain so little silica that it is sometimes disregarded; tool-steel and certain Bessemer irons are exceptions. Evaporation to dryness can then be dispensed with. The metal is simply dissolved, treated with potassium permanganate and ammonium chloride, and precipitated directly with molybdate reagent.

The following rapid method is used in many iron works' laboratories.<sup>2</sup> Five grams of steel are dissolved, oxidised with permanganate, evaporated to 25 c.c., and rinsed into a 400 c.c. conical flask. Ammonia is added very gradually, with continual agitation, in slight excess, and the solution then acidified with nitric acid until the liquid is clear, and the temperature brought up to about  $90^{\circ}$ . After adding 40 c.c. of molybdate solution, the flask is closed with a rubber stopper, wrapped in a thick cloth, and thoroughly shaken. The precipitate is allowed to settle, filtered off, and determined either by direct weighing or by titration, or by precipitation after solution, with magnesia mixture.

C. Meinecke<sup>3</sup> has proposed to dry and ignite the phospho-molybdate precipitate and to weigh it as  $24\text{MoO}_3 \cdot \text{P}_2\text{O}_5$ . This method necessitates the previous removal of arsenic.<sup>4</sup>

<sup>1</sup> *J. Iron and Steel Inst.*, 1887, ii. 365.

<sup>2</sup> *Cf.* Blair, *The Analysis of Iron and Steel*, p. 88.

<sup>3</sup> *Chem. Zeit.*, 1896, 20, 13.

<sup>4</sup> *Cf.* Frank and Henrichsen, *Stahl u. Eisen*, 1908, 28, 295.



**Oxygen.**—None of the methods hitherto proposed for determining oxygen, which may be present as ferrous or manganous oxide, in iron can be regarded as wholly satisfactory. The best available method is certainly that due to Ledebur,<sup>1</sup> in which the oxides are reduced by means of hydrogen and the resulting water collected. Irons containing enclosed slag give meaningless results by this method, since a part, at any rate, of the silicate oxygen is determined together with the oxide oxygen.

To carry out the estimation, 15 g. of fine borings, freed from adherent fatty matter by washing with alcohol and ether and dried in an exsiccator, are placed in a previously ignited porcelain boat and introduced into a combustion tube, 18 mm. wide and 500 mm. long, which is drawn out at the further end and connected to a U-tube charged with vitreous phosphoric acid; this is protected by a guard-tube containing strong sulphuric acid. A Kipp's hydrogen generator, a wash-bottle charged with alkaline lead solution, a small tube with platinised asbestos kept at dull red heat (to remove oxygen), a U-tube containing sulphuric acid and another containing vitreous phosphoric acid are placed in front of the combustion tube. Hydrogen is passed through the apparatus for an hour or two; the combustion tube is then heated up, and the boat kept at a bright red heat for thirty to forty minutes in a current of hydrogen. After allowing to cool, during which period the current of hydrogen is maintained, the hydrogen is displaced by air, and the absorption tube detached and weighed. The loss in weight of the boat serves as a check upon the oxygen absorbed as water. Owing to volatilisation of the sulphur, the former is, however, invariably greater than the latter; if the contrary should be the case, extraneous oxygen must have passed into the combustion tube.

**Slag.**—No trustworthy method is known for determining the enclosed slag in wrought iron. The following fairly satisfactory method has been worked out by Eggertz. From 2 to 5 g. of the sample are placed in a beaker with five times the weight of iodine, and the same amount of water, the whole cooled in ice, and stirred until the iron has been dissolved. The liquid is then diluted, allowed to settle, and decanted through a filter; the residue is treated with very dilute hydrochloric acid, filtered, thoroughly washed, ignited, and weighed. The carbon is thus burnt off and the slag left behind. If, as is rarely the case, the iron should contain much combined silicon, there will be an admixture of silica in the residue, which is removed by digesting it in a platinum vessel, before igniting, first with concentrated and then with dilute sodium carbonate solution.

<sup>1</sup> *Stahl u. Eisen*, 1882, 2, 193.



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## METALS OTHER THAN IRON

By Professor O. PUFAHL, Ph.D., the Royal School of Mines, Berlin. English translation revised by C. O. BANNISTER, A.R.S.M., M.I.M.M., Head of the Metallurgy Department, the Sir John Cass Technical Institute, London.

THE dry metallurgical assays described in this section are restricted to those used for silver, gold, lead, tin, and a few other metals, and which are universally recognised methods, and are not excelled by ordinary analytical methods as regards accuracy and rapidity (most silver and gold ore assays), and to such methods as are retained exclusively in practice on account of the want of good and rapid analytical methods.

The chemical examination of ores, works' products, and metals is usually preceded by some mechanical treatment, for the purpose of obtaining a true average sample, and for the preparation of the same for the ensuing assay.

### PREPARATION OF THE SAMPLE

In addition to the various types of grinding apparatus described in Vol. I., pp. 17 *et seq.*, the following may be mentioned:—

Fig. 20, a cast iron mortar with suspended pestle.

Fig. 21, a bucking plate with heavy bucking hammer.

Fig. 22, a cast iron plate with heavy hammer.

For the fine grinding of hard ore samples, a set of small cast iron rolls is often used, the ground material being received in a wooden box.

Malleable particles, such as metals, silverglance, hornsilver, left behind, on sieving pulverised ores, slags, sweeps, etc., must be kept separate, and their weight and proportion to the total weight of the sample noted. These may either be assayed separately, or a proportional amount may be added to the sieved sample taken for analysis (*cf.* Assay of Sweep, p. 126).

*Estimation of Moisture.* In powdered ore samples, as they come from the concentrating floors, the moisture must first be determined. Up to 1 kg. of the powdered ore is weighed into a series of sheet iron trays and kept at a temperature not much over 100°, the contents being

stirred with an iron spatula, until a glass plate, placed on the sample for about a minute, no longer shows a deposition of moisture, and two successive weighings agree. The dried samples are then transferred either to bottles, sheet iron boxes, or to flat porcelain plates.

The method used in some English works is to gently heat exactly 1 lb. of the sample, powdered to pass through a sieve of  $\frac{1}{16}$  inch mesh, in an iron tray or pan. When a cold glass plate or polished brass



FIG. 20.

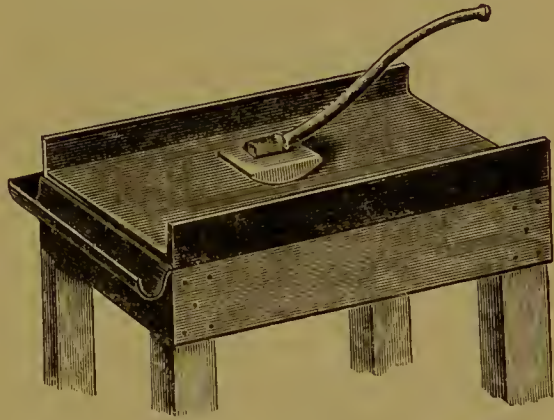


FIG. 21.

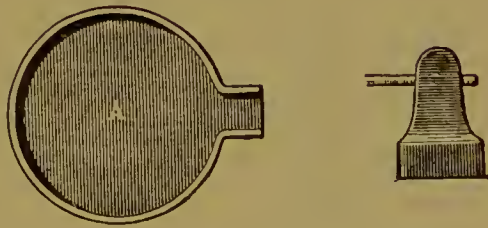


FIG. 22.

weight indicates that there is no further evolution of moisture, the whole is weighed and the result expressed in grains per seven thousand.

All samples should be retained for several months, or, at any rate, until all questions relating to sale or purchase have been settled. If the powdered samples are sent by post or rail, so that they experience considerable shaking in transit, the various constituents may become separated, owing to their different specific gravities. In such cases, the whole sample is turned out on to a sheet of paper and thoroughly re-mixed before weighing out the portion for analysis; if this be not done, serious errors may result.

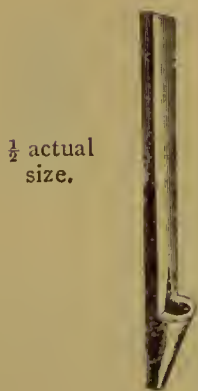
## THE SAMPLING OF METALS AND OF ALLOYS

The sampling of metals and of alloys may be effected by the dipping and granulation method.

Portions of the ingots or plates, or, in the case of the noble metals, whole ingots, are melted in a graphite crucible in a wind-furnace, the metal being covered with charcoal; the whole is stirred with an iron rod, or better, with a piece of fire-clay (Salamander rod), and a sample is taken by dipping with an iron spoon, coated with fire-clay, or by means of a charcoal rod, in which a suitable hole has been cut. This sample is then poured, in a thin stream, into an iron bucket containing water, the water being kept in a state of agitation by means of a bundle of twigs, or in the case of the charcoal sampler, the small portion removed, is flattened out.

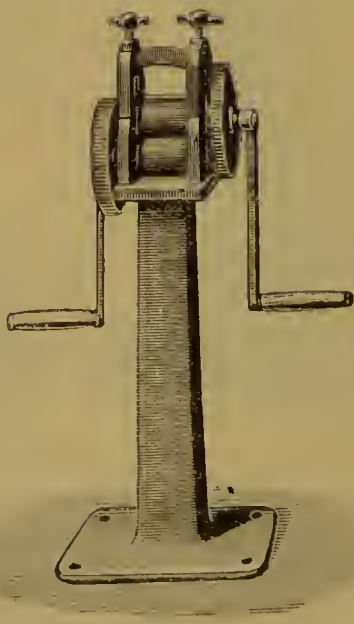
This method is unsuitable for zinc alloys on account of the unavoidable loss of zinc through volatilisation.

The ingot method of sampling is more convenient and more frequently employed than the granulation method. Samples are taken from filed or chisel-dressed portions of ingots or plates by means of a hollow punch (Fig. 23), the pieces being taken from the upper and under



$\frac{1}{2}$  actual size.

FIG. 23.



$\frac{1}{20}$  actual size.

FIG. 24.

surfaces, and from opposite upper and lower edges or corners and mixed together, or approximately equal quantities of each may be weighed. In ascertaining the fineness of ingots of noble metals, the samples from various parts are assayed separately and the mean result taken.

The samples are flattened out on a polished anvil, with a polished steel hammer, or by means of a small rolling mill (Fig. 24).



Bronzes rich in tin, samples of bearing metals, etc., which should be reduced to drillings, etc., for analysis, are often handed to the analyst in the form of small, compact pieces, which it is not possible to sample, either by filing or by drilling. In such cases, small pieces may be cut off with a cold chisel, the material being placed for the purpose on a bronze or copper plate. The chippings may be subsequently flattened, as far as possible, with a hammer.

Ingots, blocks, or large pieces of alloys that are not homogeneous (tin, lead and antimony alloys, and white metals) should be drilled in the middle and near one edge, with a small drill, the fine borings being thoroughly mixed. If the amount of drillings is considerable, say, from a number of ingots, a small ingot is produced by melting the drillings together and casting in an iron mould, which is then sampled by drilling. Or, the molten mass may be poured on to a cold, clean, iron plate, samples being subsequently cut from different parts with a pair of shears.

In the case of lead antimony alloys, according to H. Nissenson and P. Siedler,<sup>1</sup> a diagonal saw cut through a block of the alloy gives the most satisfactory sample. The sample is well mixed, reduced, and sieved, the larger particles, rich in lead, and the fine particles, rich in antimony, are separately analysed and the results adjusted. In a block of hard lead, the antimony in the upper portion was found to be 21.64 per cent., in the middle 19.98 per cent., and in the lower portion 12.08 per cent.; by the method of sampling and analysis described, the mean result obtained was 18.31 per cent.

In sampling argentiferous lead, the mode of procedure depends on the amount of silver present. For pigs or bars containing up to 20 oz. of silver per ton, chips are cut from the top and bottom of every bar with a chisel, all the chips are melted together, and a small bar is cast, from which the sample is taken. Pigs containing between 20 and 200 oz. of silver per ton are best sampled by means of a circular saw, the sawings from a diagonal cut across the pigs being collected, melted down, and cast as above. When the lead contains over 200 oz. of silver to the ton, or whenever 1 oz. of gold is present, it is necessary to melt down the whole consignment and to take a dip sample.

All brittle alloys and materials may be crushed and sieved for sampling, exactly as in the case of ores.

### *Impurities in Samples.*

Particles of iron are removed by spreading the sample on paper and passing a strong horse-shoe magnet through it.

If the drillings are made by a mechanic, it is necessary to see that neither oil nor any soapy material is used for lubricating purposes; the drillings must be received on a sheet of paper.

<sup>1</sup> *Berg u. Hütten Zeit.*, 1903, 64, 421; *J. Soc. Chem. Ind.*, 1903, 22, 1246.

Samples delivered to the laboratory in the form of drillings must always be looked upon with suspicion. Frequently the presence of pieces of other metals besides iron can be detected by the colour; these must be either picked out or evenly distributed. The presence of oil, etc., can be detected by the vapour evolved, or by the odour produced, on heating in a test tube; in addition, dirt, sand, wood splinters, and paper are often present. To clean the drillings, they should be treated in a beaker with chloroform, which is allowed to remain in contact with them for ten minutes, and then well stirred for one or two minutes, the coloured and dirty liquid poured off, and the drillings again treated with a second supply of chloroform; finally, they are washed twice with absolute alcohol and dried rapidly in a shallow porcelain dish on the water-bath. After removing any iron by means of a magnet, the fine material and sand are sieved out.

Filings should only be made with a perfectly clean or new file. Some metals and alloys rapidly foul the file.

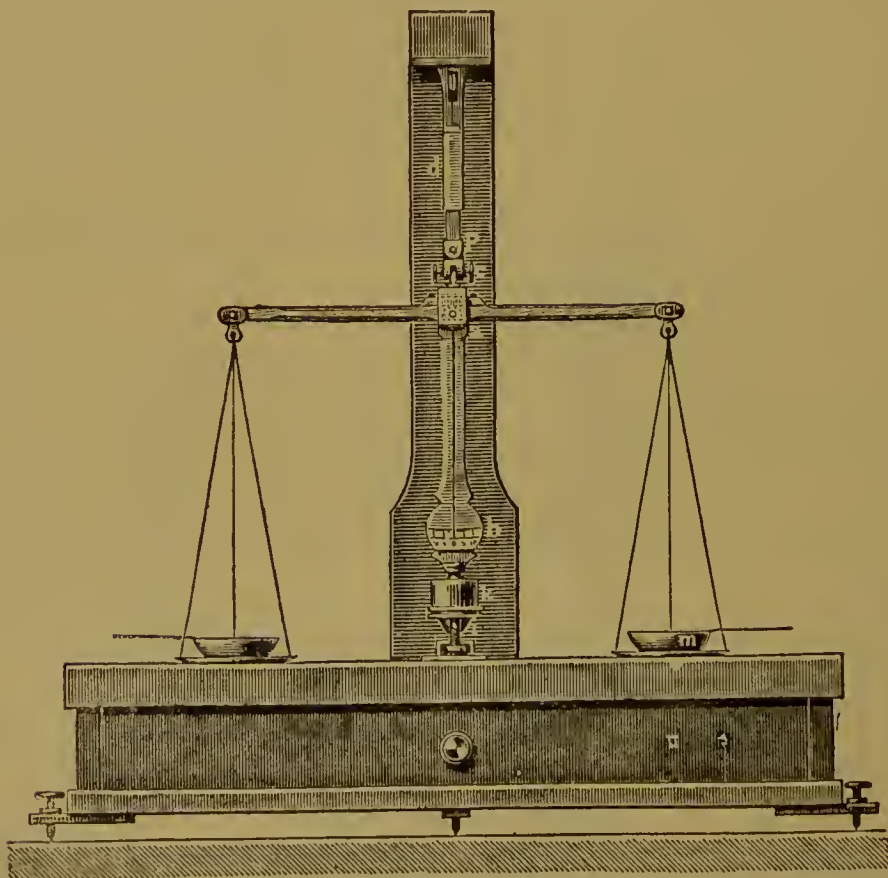


FIG. 25.

### WEIGHING

For weighing out ores, etc., for analysis, any sufficiently delicate balance may be used. In assay laboratories, a simple quick-arrest ore

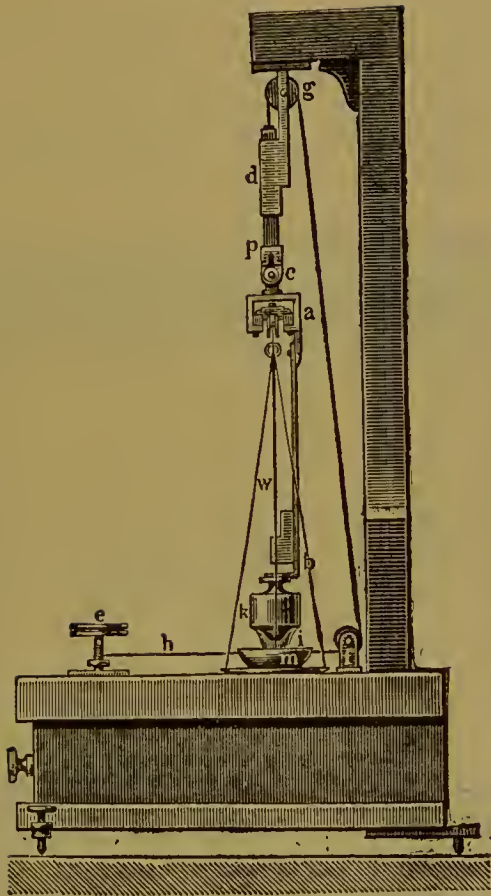


FIG. 26.

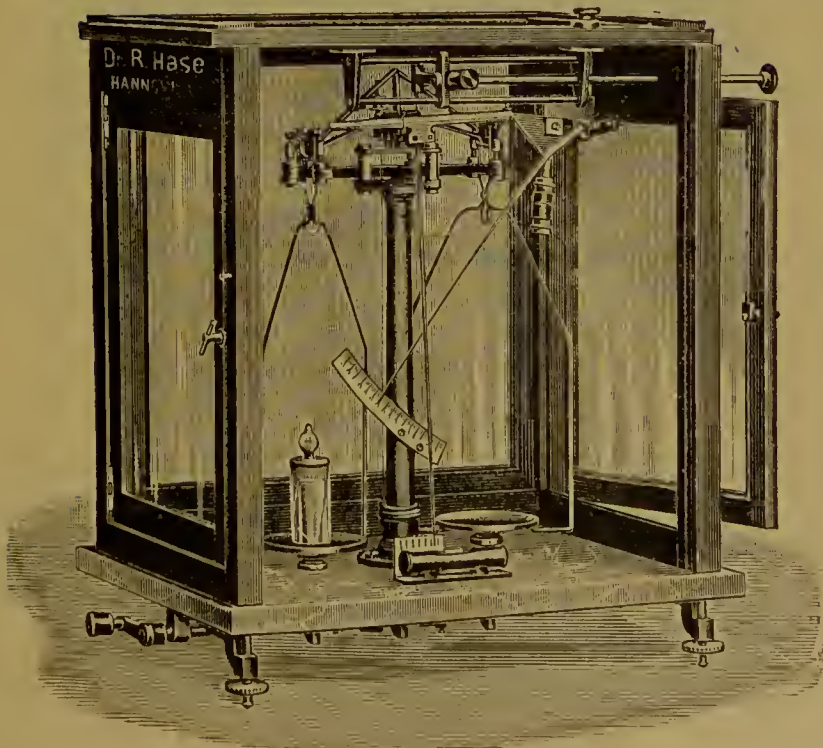


FIG. 27.



balance (Figs. 25 and 26), provided with removable nickel pans, and sensitive to 1 mg., with a load of 50 g., suffices.

Fig. 27 shows a good combination of an ore tare balance and a delicate balance devised by R. Hase<sup>1</sup> (*see also*, Vol. I., p. 20).

For weighing noble metals and their alloys in mints, etc., assay

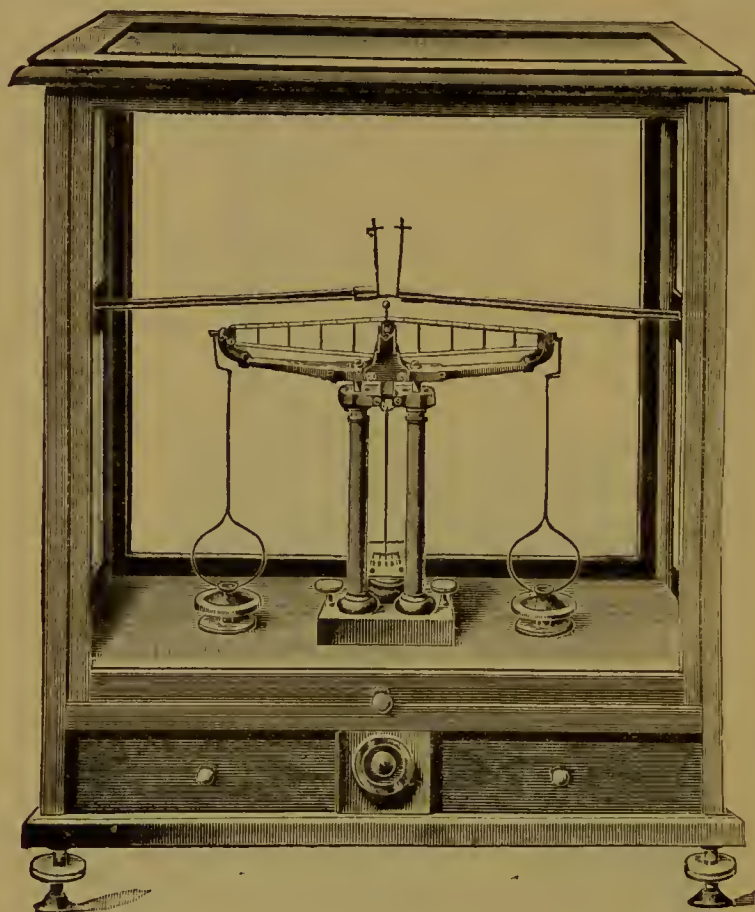


FIG. 28.

balances (Fig. 28) are employed, which are sensitive to 0.05 to 0.01 mg., with a load of 2 g.

## SILVER

The materials which have to be assayed for their value in silver include the following:—Silver-bearing ores, metallurgical products (such as furnace lead, products of the desilverisation of lead, skimmings, litharge, test-hearth material, lead and copper mattes, speiss, scoriæ, flue-dust, slags, blister copper, crude silver, refined silver), cement silver, silver sulphide, amalgams, and residues from amalgamation and other extraction processes, silver alloys and sweeps from their manufacture, silver-plated goods, plating liquors, etc.

<sup>1</sup> *Z. angew. Chem.*, 1898, **11**, 736.



In most cases the dry method of assay is to be recommended; the wet method is employed for silver itself (crude and refined silver, bar silver), silver alloys, such as bullion, etc., and silver baths, the strength of which can be most accurately determined by precipitation or by titration. Occasionally the wet and dry methods are combined.

### Silver Ores.

The most important silver ores are:—

*Native silver*, with not infrequently small quantities of gold, mercury, copper, iron, arsenic, and antimony.

*Antimonial silver*, containing up to 94 per cent. of silver.

*Argentite*, or *silver glance*,  $\text{Ag}_2\text{S}$ , containing 87.1 per cent. of silver.

*Polybasite*,  $9(\text{CuAg})_2\text{S}$ ,  $(\text{SbAs})_2\text{S}_3$ , with 72 per cent. of silver.

*Stephanite*,  $5\text{Ag}_2\text{S}$ ,  $\text{Sb}_2\text{S}_3$ , with 68 per cent. of silver.

*Pyrargyrite*,  $3\text{Ag}_2\text{S}$ ,  $\text{Sb}_2\text{S}_3$ , with 59.8 per cent. of silver.

*Miargyrite*,  $\text{Ag}_2\text{S}$ ,  $\text{Sb}_2\text{S}_3$ , with 37.2 per cent. of silver.

*Proustite*,  $3\text{Ag}_2\text{S}$ ,  $\text{As}_2\text{S}_3$ , with 65.5 per cent. of silver.

*Stromeyerite*, or *silver copper glance*,  $\text{Cu}_2\text{S}$ ,  $\text{Ag}_2\text{S}$ , containing 53 per cent. of silver.

*Freieslebenite*,  $3\text{Ag}_2\text{S}$ ,  $4\text{PbS}$ ,  $3\text{Sb}_2\text{S}_3$ , containing 23 per cent. of silver.

*Silver amalgams*, containing up to 95 per cent. of silver.

*Kerargyrite*, or *horn silver*,  $\text{AgCl}$ , containing 72.5 per cent. of silver.

*Bromite*,  $\text{AgBr}$ , containing 57.4 per cent. of silver.

*Embolite*, which includes isomorphous mixtures of chloride and bromide of silver, varying in composition from  $\text{AgCl} + 3\text{AgBr}$  to  $\text{AgBr} + 3\text{AgCl}$ , and which may contain up to 70 per cent. of silver.

*Iodite*,  $\text{AgI}$ , containing 46 per cent. of silver.

*Tetrahedrite*, or *fahl ore*, which is a mixture of antimony or arsenic sulphide, or both, with sulphides of silver, copper, zinc, iron, or mercury, and which may contain from a fraction of 1 per cent. up to 31 per cent. of silver. When antimony and arsenic are both present, the silver seldom amounts to 1 per cent.

A considerable proportion of the silver produced is obtained from argentiferous galena and other lead and copper ores, and not from silver ores proper.

### DRY METHODS OF SILVER ASSAY

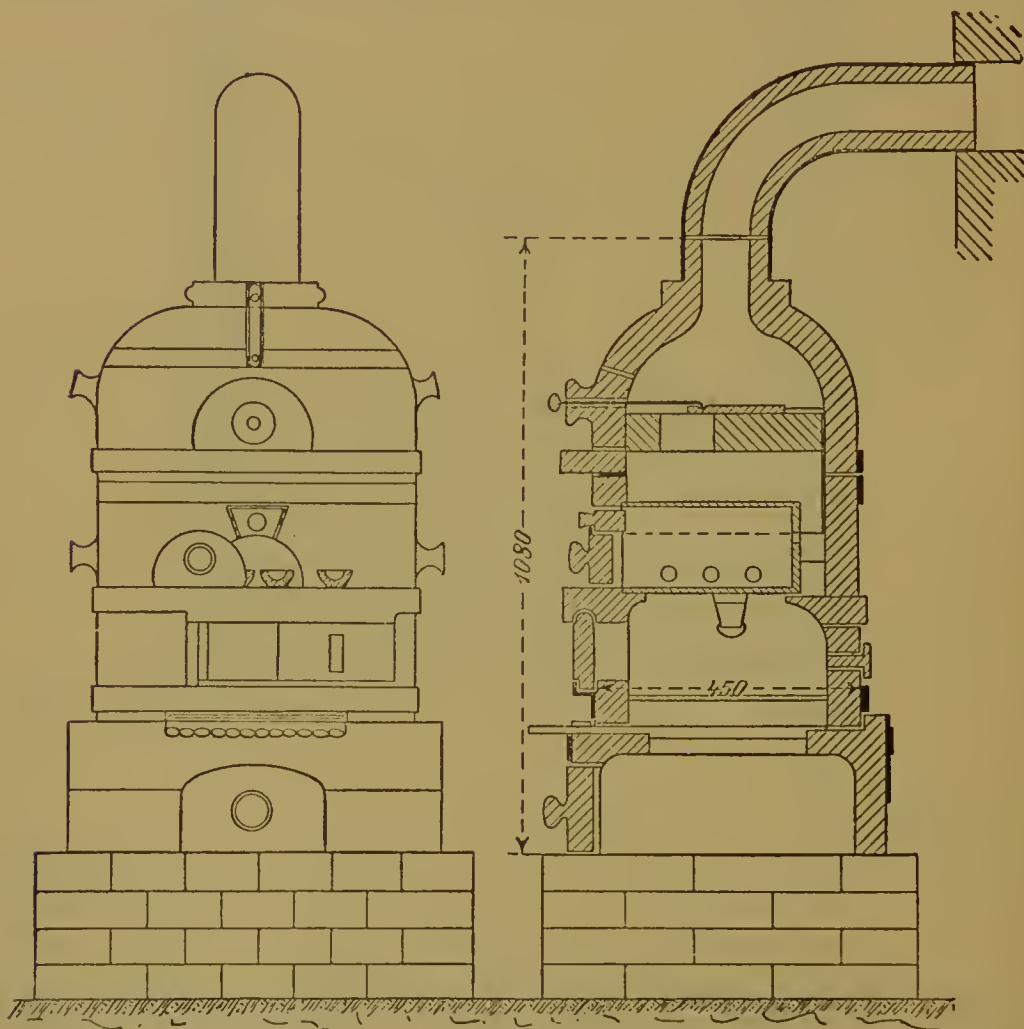
The dry methods of silver assay consist in dissolving out the silver (and gold) by means of pure lead in a melting operation, the lead

button obtained being subsequently cupelled. Two methods are in use for producing the lead button, viz., the scorification and the pot or crucible methods.

# I.—DRY ASSAY FOR ORES, ETC. (excluding silver alloys)

## 1. The Extraction with Lead.

(a) **Scorification.**—The process is carried out in a muffle furnace, heated with coal, coke or gas (or with benzine, petroleum, etc.), and



FIGS. 29 and 30.

connected with a chimney. In many assay offices gas muffles are exclusively employed for scorifications and cupellations; the advantages are cleanliness and exact regulation of temperature, with consequently smaller silver losses in the assay. A portable form of muffle furnace, as used at Freiberg, for coal or coke, is shown in Figs. 29 and 30.

*Manipulation.* Usually from 4 to 5 g. of the finely powdered sample are weighed out on a balance such as that shown in Fig. 25, p. 94; of

materials rich in silver less may be taken, and of very poor material, from three to five times as much, but, in the latter case, correspondingly large scorifiers must be used.

The necessary quantity of finely granulated assay lead is measured in a spoon of known capacity; about one-half is well mixed with the powder in a scorifier, and the remainder is evenly spread on the top. Finally, if necessary, a little borax is added. If much silica is present in the ore, slagging will be facilitated by an addition of litharge, free from silver.

Where the silver content is under 0.4 per cent., it is usual to weigh out two lots and to carry out two scorifications; with a content of 0.4 to 0.79 per cent. three, and with over 0.8 per cent. four scorifications are made, the actual result being taken from the mean weight of all the silver beads, weighed separately.

If the approximate silver content of the material to be assayed is not known, a preliminary test is made. This method of working is founded on the fact that the distribution of silver in rich ores is not uniform.

The quantity of assay lead required depends on the character of the material. Pure lead ores require only six times their weight of lead; the same holds good for hard-lead.

Materials containing fair amounts of iron and zinc require considerably more lead, from ten to fifteen times the weight of the ore taken; those containing much copper, nickel, or tin require up to thirty times their weight. Similarly, the quantity of borax needed varies; this must be anhydrous and powdered. Its purpose is to increase the fluidity of the slags in the case of materials containing much gangue and metallic oxides, difficultly soluble in lead oxide, and it should be added in small quantities from time to time, as required.

The following table will be a useful guide as to the amount of lead and fluxes necessary with different classes of ores and materials:—

Material.	Amount.	Lead.	Flux (Borax).
	g.	g.	g.
Siliceous . . . ores	5	60	0.5
Ferruginous . . . "	5	50	2.0
Pyritic . . . "	5	70	1.0
Cupreous . . . "	5	80	1.0
Antimonial . . . "	3	80	{ 1.0 Borax.
Stanniferous . . . "	3	60	{ 1.0 Sod. carb.
Lead speiss . . . .	5	60	{ 2.0 Borax.
Blende . . . . .	5	70	{ 4.0 Sod. carb.
Slags . . . . .	5	60	1.0
Brass and bronze . . .	3	100	1.0
German silver . . . .	3	110	1.3
Copper . . . . .	3	60	1.5
			0.3

The scorifiers (Fig. 31) are made of best fire-clay, and must withstand sudden changes of temperature and, to a certain extent, the corrosive action of molten lead oxide. The size of scorifiers used is governed by the size of the muffle, as it is desirable to make as many scorifications at one time as possible. If it is desired to mark them, red ruddle may be used, with which they are marked on the outer surface with numbers or streaks. The scorifiers, with contents, are placed, by means of the tongs (Fig. 32) in the muffle, which has already been brought to a bright red heat, and the door is closed.

During the first or heating-up period a high temperature is especially necessary, if the material contain iron, zinc, tin, copper, or nickel and cobalt. When, after ten to fifteen minutes, the scorifiers have attained a bright heat, the contents are molten, lead fumes are copiously given off, and a ring of molten litharge shows itself; the muffle is then opened. During this second, or slagging, period, the current of air, passing continuously into and through the muffle, effects a rapid oxidation of the material in the scorifiers; this oxidation is partly



FIG. 31.



FIG. 32.

direct and partly brought about through the agency of the lead oxide, which acts on the undecomposed metallic compounds. Sulphur and arsenic to a great extent volatilise, the metallic oxides and the gangue dissolve gradually in the molten litharge and borax, and the noble metals are retained by the lead, which may also take up, at the same time, certain quantities of copper, tin, bismuth, iron, arsenic, and antimony. While scorification is proceeding, the temperature of the muffle is lowered somewhat.

As scorification progresses, the litharge ring gradually encroaches more and more on the surface of the lead button, until ultimately it closes completely over it. The muffle is then again closed, the temperature raised, so that the contents of the scorifier may become thinly fluid, and a small quantity (0.1 g.) of powdered anthracite is sprinkled over the surface; this reduces a little lead, which in turn cleans the slag, carrying the precious metals into the main button. After a further ten to fifteen minutes, the scorifiers are removed by the aid of scorifier tongs (Fig. 33) and emptied into moulds (Fig. 34), which have been black-leaded and warmed.

When cold, the slag is removed from the lead button by hammering on an anvil, the lead beaten into the form of a cube, the edges and corners



being blunted by gentle blows, and the cube cleaned by brushing. Should the lead appear to be brittle, owing to the presence of an appreciable amount of arsenic or antimony, it should not be directly cupelled (*cf.* Cupellation, pp. 105 *et seq.*); it is better, in such cases, to scorify again with an equal weight, or double the weight, of assay lead.

Lead buttons, weighing more than 30 g., should preferably be re-scorified in correspondingly small scorifiers, as the unavoidable loss of silver on cupellation is then less than if directly cupelled. If scorification be carried to an excessive point, all the lead oxidises and silver and gold pass into the slag.

If the material under treatment is so poor in silver that only a very small silver bead is obtainable from one lead button, concentration is



FIG. 33.



FIG. 34.

resorted to, *i.e.*, the lead buttons from several scorifications are re-scorified together, and this may be repeated until the silver, from a very considerable quantity of ore, has been collected into two lead buttons, each weighing about 30 g. This is the method adopted, for example, with blister copper and other materials, usually very poor in silver.

In the "Staatshüttenlaboratorium" at Hamburg,<sup>1</sup> cupreous silver sulphide (obtained in silver extraction processes) is scorified twice; the weight taken is not over 2 g. At the same laboratory, in assaying the dust from silver burnishing, only 1 g. is taken for each of five to ten scorifications, and the combined lead buttons are then concentrated by scorification.

(b) **The Pot or Crucible Assay.**—In this method the silver and gold from a large quantity of ore is collected in a lead button in one melt, and the button is then cupelled. The method is particularly suitable for ores containing tellurium or horn silver, and also for very poor ores, slags, tailings, and the various residues and sweeps, especially when they contain carbonaceous material.<sup>2</sup>

Tolerably smooth fire-clay crucibles are employed for the fusion. The mixture of ore, etc., with litharge or red lead, fluxes, and reducing material is introduced, generally with a piece of hoop iron also, and melted in a wind-furnace heated with charcoal or coke, or sometimes in a gas-furnace, the temperature being gradually raised, until the melt

<sup>1</sup> Private communication from the director, W. Witter, to Prof. Pufahl.

<sup>2</sup> *Cf.* A. Goerz, *Berg u. Hütten. Zeit.*, 1886, 45, 441.

is tranquil. The silver content of the litharge or red lead must be taken into account.

The lead oxide decomposes any metallic sulphides, etc., and the metallic lead, reduced by the carbonaceous matter and sulphides, collects the silver and gold.

Materials rich in sulphur, arsenic, antimony, or zinc, are preferably subjected to a preliminary roasting on roasting dishes or trays (Figs. 35 and 36), otherwise appreciable quantities of silver may pass into the slag.

It is not possible to specify a fusion mixture equally suitable for all cases, although the following mixture will frequently be found satisfactory: 25 g. ore, 30 g. sodium carbonate, 40 g. red lead, and 1.5 g. charcoal are mixed in a sufficiently large crucible by means of a spatula, and 10 g. of anhydrous borax are put on the top. A piece of hoop iron is then inserted, the crucible covered, and placed in the wind-furnace.

The heating must be gentle for the first quarter of an hour, incipient fusion or "fritting" only taking place, otherwise there is a liability of the

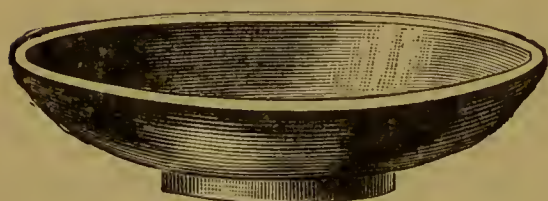


FIG. 35.



FIG. 36.

litharge melting and running down to the bottom of the charge, leaving the precious metals behind and causing a heavier loss in the slag; then the damper is drawn and the heating continued for twenty minutes, until the melts are tranquil. The iron strips are then removed, the crucibles withdrawn from the furnace with bent-nosed tongs, and the contents poured into moulds as before. After cooling, the lead buttons are removed, freed from slag, and brushed ready for cupellation (*cf.* Cupellation, pp. 105 *et seq.*). If the charges be not too difficultly fusible, the melts may be made in a muffle furnace. In this case, the crucibles are placed well back in the muffle, and, after a quarter of an hour's heating, a good layer of well-burnt wood-charcoal is placed in front of them and the muffle closed.

On mines where a large number of assays have to be made on the same class of material, it is usual to prepare a stock of mixed fluxes, made up in proportions to suit the character of the ore, but in many laboratories the nature of the ores varies considerably, and the fluxes should then be made up accordingly. The following charges, given in grams and assay ton weights,<sup>1</sup> will be found useful:—

<sup>1</sup> For explanation of assay ton weights, *cf.* p. 107.

Table of Charges for the Dry Assay of Silver Ores in Grams.

	Siliceous.	Basic.	Pyritic.	Cupriferous Pyritic.
Ore. . . . .	25	25	25	20
Red lead. . . . .	30	30	40	60
Charcoal. . . . .	1.5	2 to 3	...	...
Sodium carbonate . . .	40	20	30	20
Borax . . . . .	5	20	15	20

Table of Charges for the Dry Assay of Silver Ores  
in Assay Tons.

	Siliceous.	Basic.	Pyritic.	Cupriferous Pyritic.
Ore. . . . .	1.0	1.0	1.0	0.5
Red lead. . . . .	1.0	1.0	1.25	2.0
Charcoal. . . . .	0.05	0.06 to 0.1	...	...
Sodium carbonate . . .	1.0	0.75	1.0	0.5
Borax . . . . .	0.2	0.75	0.5	0.5

[*Note.*—Charges for ores containing stibnite, arsenical pyrites, cassiterite, tellurides, etc., are given under "Gold," pp. 127 *et seq.*]

In the case of poor quartzose or similar material, up to 500 g. are taken for each melt. A good mixture consists of one and a quarter to twice as much anhydrous sodium carbonate as ore, 30 g. of red lead and 1.5 g. of powdered charcoal. The mixture is added gradually from a metal scoop (Fig. 37), on account of its foaming during melting, and borax, up to 25 per cent. of the weight of ore, is added, little by little. In the case of material containing an excessive amount of iron, more charcoal is needed, as a considerable quantity is required for reducing ferric to ferrous oxide; otherwise none would be available for producing lead. Further, it is advantageous to sprinkle a mixture of litharge and argol (or a little granulated lead) on the tranquil surface of the melt.

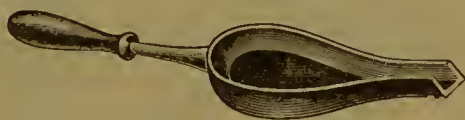


FIG. 37.

In the assay of lead slags (using 50 g. or more of material) with more protracted fusion with sodium carbonate, borax and argol, granulated lead is added, or may be sprinkled over the surface after melting down.

Lead ores are often assayed in thick wrought iron crucibles (*cf.* Lead assay, pp. 220 *et seq.*), and the lead button obtained is used for the silver determination. In this case from 15 to 20 g. of litharge are added to the ore and the whole melted down; litharge, flux, and charcoal are







flux (consisting of fourteen parts of anhydrous sodium carbonate, eight parts of fused borax, and two parts of argol) are added and heating continued until the melt is tranquil; the charge is then poured into a warm iron mould and the cleaned bead cupelled. The method is quick, and gives good results.

Details of laboratory, crucible, and muffle furnaces, together with specifications, have been described by G. T. Holloway.<sup>1</sup> The wind-furnaces used at the Royal School of Mines, Berlin, are shown in Figs. 38 and 39.

In the assay of very rich ores, a notable amount of silver passes into the slag. To recover this, the melt is poured into a warm mould (Fig. 40), the slag collected and re-melted in the same crucible, with borax, argol, and litharge. If, however, the materials under investigation are poor, the loss of silver in the slag is negligible.

## 2. Cupellation.

The separation of silver and any accompanying gold from the lead obtained in the scorification process, or in the pot assay, is effected by oxidation on a cupel made of bone-ash, magnesia, or some porous mixture (Fig. 41), at a bright red heat in a muffle furnace. The porous refractory cupel gradually absorbs the lead oxide formed, and finally a bright button of silver remains behind.

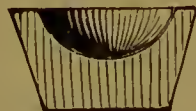


FIG. 41.

The burnt bone-ash, used for making cupels, is ground and sieved to about the fineness of wheat meal. After moistening with a little water, containing 2 per cent. of potassium carbonate, the bone-ash is shaped to the requisite form in a cupel mould, preferably of brass or of gun metal. The cupels are kept on shelves in the furnace room and are thoroughly air-dried; they should be kept for several months before use. Cupels can also be made by means of a mechanical press.<sup>2</sup> Many brands of manufactured cupels are now on the market, and are largely used by assayers.

The ordinary cupel holds from 15 to 30 g. of lead, and is capable of absorbing all the lead oxide produced from this; larger cupels are sometimes employed, as, for instance, for lead containing but little silver.

*Manipulation.* The cupels are first gradually heated in the muffle, in order to completely drive off moisture and carbonic acid. They should be placed well back in the muffle, in one or more rows, before lighting up, and should be kept at a bright red heat for at least a quarter of an hour before use; otherwise the lead may spit on melting down on the cupel and so spoil the whole series.

<sup>1</sup> *Trans. Inst. Min. and Met.*, 1906-7, 16, 341.

<sup>2</sup> Cf. Muspratt-Stohmann's *Handbuch der technischen Chemie*, 4th edition, iii., p. 1721.

After a thorough heating, the cupels are drawn forward, with iron tongs, on the bottom of the muffle, and are left in the front of the muffle in a row. The lead buttons, brushed, and blunted on the edges and corners, are carefully transferred to the cupels by means of the bent-nosed cupel tongs (Fig. 42), the front row being supplied first.

The muffle is then closed and the lead allowed to melt, when a dark skin first forms on the surface. As soon as this disappears and the molten lead, which acquires a bright convex surface, begins to give off a considerable quantity of lead fume, the muffle door is opened somewhat and cupellation proper commences.

The oxidation takes place rapidly. Drops of molten litharge form and, floating over the surface of the lead, are absorbed by the porous cupels. If the temperature be not too high, the lead smoke curls upwards and gradually produces a dark red crystalline and leafy deposit of litharge on the inner edges of the cupels (this deposit is yellow when cold). At the same time, the drops of litharge on the convex surface of the lead unite together, forming a litharge edging to the lead.

When the muffle temperature is too high, this is indicated by the smoke rising vertically and by the absence of the litharge ring referred



FIG. 42.

to. If the temperature be too low, the lead smoke keeps low over the cupels, which themselves appear somewhat dull; in such cases, the temperature must be immediately raised, otherwise "freezing" may take place.

As cupellation proceeds, the litharge drops will gradually increase, and the fusing point of the alloy, as it becomes richer in silver, will rise. The temperature becomes lowered by the continuous current of air passing into the muffle, consequently the door should be closed, and the temperature increased. Finally, the litharge drops disappear from the lead, as it gets smaller and smaller, a revolving iridescent skin of oxide is noticed for a short time, if the bead be not very small, and then suddenly the bead "brightens" before solidifying.

Cupels, containing very small silver beads, that weigh a few milligrams only, may be removed from the muffle immediately after the solidification of the beads; but in the case of larger beads, the cupels should be gradually drawn forward, to allow the silver to set slowly. If this be not done, there is a danger of silver being lost through "spitting" of the bead, owing to the sudden escape of absorbed oxygen through the prematurely formed solid crust. Beads, which have "spit," are consequently, as a rule, lighter than those which have not, and should not be taken into account in arriving at the result of the assay.

By covering the cupels with inverted cupels slow cooling can be ensured, even when they are immediately removed from the muffle.

The small spherical beads and the larger hemispherical beads are removed from the cupels by means of pliers, squeezed to remove adhering particles torn from the cupel, well brushed on the under side with a stiff prill brush, and placed on a sheet of lead, about the size of a playing-card and provided with a number of small depressions. The upper surface of beads, from a thoroughly satisfactory cupellation, is bright, and of a whitish colour, the under side matt and silver-white. If "brightening" has taken place at too low a temperature in contact with litharge, the bead is matt and yellowish on its upper surface, owing to the presence of a thin layer of oxide of lead; such beads are too heavy and must be rejected, or re-cupelled with a small quantity of assay lead.

The beads never consist of absolutely pure silver; they contain from 0.2 to 0.3 per cent. of lead, with traces of copper. These impurities serve, to a certain extent, to compensate for the unavoidable loss of silver during cupellation.

Any gold and platinum, contained in the material assayed, is collected quantitatively in the silver bead and is determined therein (*cf.* Gold, p. 128).

The beads are weighed on a delicate assay balance (Fig. 28, p. 96), or on a chemical balance sensitive to 0.1, or, better to 0.05 mg.

When many assays of silver or gold ores have to be made, it is usual to work with "Assay Ton" weights. Since there are 32,666.6 oz. troy in a ton of 2240 lb., if the standard weight be made 32.66 g., each milligram of silver or gold obtained from this quantity will be equivalent to 1 oz. per ton. In the case of the short ton of 2000 lb., now largely used, the assay ton = 29.16 g.

Whenever these special weights are not used, the percentage value is first obtained, and from this the ounces, etc., per long or short ton can readily be calculated from the table on p. 108.

The individual beads obtained in assaying argentiferous lead ores usually agree well with each other in weight, those from silver ores proper (especially native silver, silver glance or horn silver) frequently show appreciable variations, on account of the uneven distribution of the silver in the ore. In these cases, it is necessary to carry out a considerable number of assays and take the mean. Loss of silver occurs to a certain extent during slagging, in both the scorification and the pot assay,<sup>1</sup> but the losses during cupellation are much greater, as silver oxide is carried into the cupel along with the litharge, and this is especially the case with very porous cupels; further, some silver volatilises along with the lead. It is to be noted that if finished assays be left too long in the muffle, volatilisation of silver may take place.

<sup>1</sup> H. Rössler, *Z. angew. Chem.*, 1888, 20, 567; *J. Soc. Chem. Ind.*, 1888, 7, 869; 1889, 8, 137.



Table for computing the Troy Weight of Gold or Silver  
per Long and Short Ton.

Per cent.	Per ton of 2240 lb.			Per ton of 2000 lb.			Per cent.	Per ton of 2240 lb.			Per ton of 2000 lb.		
	oz.	dwt.	gr.	oz.	dwt.	gr.		oz.	dwt.	gr.	oz.	dwt.	gr.
0·0001	...	...	16	...	...	14	0·06	19	12	0	17	10	0
0·0002	...	1	7	...	1	4	0·07	22	17	8	20	8	9
0·0003	...	1	23	...	1	18	0·08	26	2	16	23	6	17
0·0004	...	2	15	...	2	8	0·09	29	8	0	26	5	0
0·0005	...	3	6	...	2	22	0·1	32	13	8	29	3	8
0·0006	...	3	22	...	3	12	0·2	65	6	16	58	7	0
0·0007	...	4	14	...	4	2	0·3	98	0	0	87	10	0
0·0008	...	5	5	...	4	16	0·4	130	13	8	116	14	0
0·0009	...	5	21	...	5	6	0·5	163	6	16	145	17	0
0·001	...	6	13	...	5	20	0·6	196	0	0	175	0	0
0·002	...	13	2	...	11	16	0·7	228	13	8	204	4	0
0·003	...	19	14	...	17	12	0·8	261	6	16	233	7	0
0·004	1	6	3	1	3	8	0·9	294	0	0	262	10	0
0·005	1	12	16	1	9	4	1·0	326	13	8	291	14	0
0·006	1	19	5	1	15	0	2·0	653	6	16	583	8	0
0·007	2	5	18	2	0	20	3·0	980	0	0	875	2	0
0·008	2	12	6	2	6	16	4·0	1306	13	8	1166	16	0
0·009	2	18	19	2	12	12	5·0	1633	6	16	1458	10	0
0·01	3	5	8	2	18	8	6·0	1960	0	0	1750	4	0
0·02	6	10	16	5	16	16	7·0	2286	13	8	2041	18	0
0·03	9	16	0	8	15	0	8·0	2613	6	16	2333	12	0
0·04	13	1	8	11	13	8	9·0	2940	0	0	2625	6	0
0·05	16	6	16	14	11	16	10·0	3266	13	8	2916	14	0

When very great accuracy is desired in the assaying of ores, etc., the cupels are broken up and powdered and the lead reduced and cupelled (*cf.* Gold, p. 128); in this way most of the silver, etc., is recovered in the form of a weighable bead.

The determination of silver in impure silver precipitates (chloride, iodide, or sulphide), such as are obtained in the extraction of low grade ores, burnt pyrites, etc., is best effected by scorification with lead, followed by cupellation of the button so obtained.

In the American method of C. Whitehead and T. Ulke, several grams of assay lead are wrapped in the dried filter paper, and this is immersed in molten lead, ready prepared to receive it, on a scorifier.

**Combined Lead and Silver Assay.**—The silver content of litharge scums, furnace hearth, and other oxidised products is determined by reducing the lead (*cf.* Lead assay, pp. 220 *et seq.*), and then cupelling. The lead buttons obtained from galena by fusion with sodium carbonate (*cf.* Lead assay, p. 220) are also cupelled to ascertain the silver content.

Plattner's quantitative blowpipe assay<sup>1</sup> is of special importance for prospectors; in sufficiently expert hands the method gives toler-

<sup>1</sup> *Manual of Qualitative and Quantitative Analysis with the Blowpipe*, Plattner. English translation by H. B. Cornwall, 1902.



ably accurate results, working on the small quantities of material (0.1 g.).

**Combined Wet and Dry Silver Assay.**—This method is particularly suitable for ores, mattes and alloys containing large quantities of copper. From 10 to 25 g. of the material to be assayed are weighed out and treated with nitric acid, the whole heated until quite decomposed and taken up with water. A solution of 20 g. of lead acetate in water is then added, followed by a small quantity of sodium chloride solution to precipitate the silver and a portion of the lead present. The liquid is heated, then allowed to cool, filtered, and the residue and precipitate washed once with cold water. The filter paper and residue are dried, and the whole mixed with 25 g. of red lead, 20 g. of sodium carbonate, and 1.5 g. of charcoal. This charge is run down in a clay crucible as usual, and the lead button obtained, cupelled (Bannister).

**Complete Analyses** of silver ores proper (ruby silver ore, silver glance, antimonial silver, stephanite, polybasite, fahl ores, etc.) are not required for technical purposes. If the silver only is to be determined, 1 g. of the powdered ore is dissolved in a mixture of nitric and tartaric acids (10 c.c. nitric to 2 g. tartaric acid), and the silver precipitated with hydrochloric acid. The precipitate is filtered off, washed with water containing a little nitric acid, until free from hydrochloric acid, and then dried in an air-bath. Fairly large quantities of silver chloride are weighed as such. The silver chloride is turned out on to glazed paper, the filter paper burnt, its ash transferred to a weighed porcelain crucible, treated with a few drops of nitric acid and, subsequently, a drop or two of hydrochloric acid, while it is heated on a water-bath; after the acid has been evaporated off, the bulk of the silver chloride is added, the crucible lid put on, and the crucible heated to incipient melting of the chloride. Should the silver chloride amount to only a few milligrams or centigrams, however, the filter paper with the whole of the precipitate is, after drying, placed in a weighed Rose's crucible, the paper burnt, the crucible lid put on, the chloride reduced by heating for ten minutes in a current of hydrogen or coal gas, and the resulting silver weighed.

**Electrolytic Methods,**<sup>1</sup> for the estimation of silver in ores, are seldom used.

## II.—THE ASSAY OF SILVER ALLOYS

The poorer silver alloys are assayed in the dry way; in the case of the richer alloys, the dry assay is frequently used as a preliminary determination only to ascertain the approximate silver content previous to carrying out an accurate estimation in the wet way.

<sup>1</sup> Cf. Kiliani, *Berg u. Hütten. Zeit.*, 1883, 42, 400.

## A. DRY ASSAYS

1. **Furnace Lead.**—If not very impure, the crude lead, obtained in the furnacing of lead ores, may be directly cupelled in quantities of from 20 to 50 g. Should, however, the impurities be considerable, the lead is first scorified with an equal or double weight of assay lead. Rich silver-lead is cupelled directly. Desilverised lead (soft lead) is first scorified in quantities of 100 g. and upwards, and the subsequent lead button, of about 30 g., cupelled.

2. **Hard Lead** (antimonial lead) and the Mexican "Peñoles" lead, rich in silver and containing a considerable amount of antimony and arsenic, is first scorified with double its weight of assay lead, and concentrated, etc.

3. **Argentiferous Blister Copper and Refined Copper** require to be scorified with twenty times their weight of assay lead, and concentrated previous to cupellation.

4. **Silver Amalgam.**—According to Kerl,<sup>1</sup> most of the mercury should be distilled off in a potash-glass retort, if the amalgam be rich in mercury; the residue is then scorified with from six to eight times its weight of assay lead.

Solid amalgam is heated very gradually on a cupel up to a bright red heat in the course of an hour and a half, in a muffle, the cupel being covered with a second inverted cupel; the residue is cupelled with from six to eight times its weight of assay lead.

5. **Zinc Skimmings**, containing lead, zinc, and silver, from the Parkes desilverising process, are first scorified with sixteen times their weight of assay lead.

The following combination of wet and dry methods is described by L. Campredon.<sup>2</sup> A representative sample of 25 g. weight is dissolved in a mixture of nitric and tartaric acids, the silver and a considerable quantity of lead precipitated with hydrochloric acid, and the washed and dried precipitate fused with the addition of 20 g. of litharge and the necessary flux; the button of lead thus obtained is cupelled.

6. **Crude Silver** (containing 95 to 96 per cent. of silver), **Refined Silver** (containing 97 to 99.5 per cent. of silver), and **Cement Silver** are assayed by wet methods only (*cf.* pp. 112 *et seq.*).

7. **Bullion and Silver containing Copper.**—Before the introduction of the Gay-Lussac wet method of assay, such alloys, even those richest in silver, were assayed exclusively in the dry way by taking an accurately weighed amount (two quantities each of 0.5 g.), and cupelling with a sufficiency of assay lead on a cupel of pure bone-ash.

<sup>1</sup> *Metallurg. Probierekunst*, 2nd edition, p. 301.

<sup>2</sup> *Guide pratique du Chimiste Métallurgiste et de l'Essayeur*, 1898.

The unavoidable loss during cupellation was carefully determined,<sup>1</sup> and by making corrections, on the basis of such losses, the actual fineness could be arrived at with tolerable accuracy.

*Preliminary Assay.* As the amount of lead needed depends on the percentage of copper and other metals (other than silver and gold) in the alloy, the approximate fineness is first ascertained either by the touchstone, or by cupelling 0.1 to 0.2 g. with eighteen times its weight of assay lead.

Streaks are made with the alloy on a touchstone of black basaltic stone, and, adjoining these, other streaks are made with test needles of known fineness; by a comparison of the colours, after treatment with acid, an approximate result is arrived at. The presence of zinc in silver alloys considerably affects the streak, and gives rise to high results.

According to Rössler, it is possible to ascertain by means of the streak whether or not an alloy contains silver. The streak is treated with one or two drops of pure concentrated nitric acid, and, when it has disappeared, leaving no trace of turbidity, a drop of hydrochloric acid produces the characteristic white precipitate, or a turbidity, if silver is present. Lead may also give a turbidity, but this disappears on the addition of a little water.<sup>2</sup> Alloys, poor in silver (400/1000 and under) require eighteen to twenty times their own weight of assay lead for cupellation; alloys of approximately 500/1000 require sixteen, 700/1000 require twelve, 800/1000 require ten, 900/1000 require eight, and 950/1000 and over require four times their own weight. In mint laboratories this assay lead is kept in standard lumps or pellets.

*The Assay Proper.* From two to four cupels, ready heated, are drawn forward in the muffle, the assay lead introduced, and the muffle closed; as soon as the lead has "uncovered," the alloy (0.5 g. if fine silver, or 1 g. if 800/1000), wrapped in sheet assay lead, is added with the aid of the tongs, and the muffle again closed. After about a couple of minutes, when complete fusion has taken place, the muffle is opened, and cupellation proceeds. The litharge ring appears gradually, but seldom litharge crystals. Finally, the bead becomes iridescent, and brightens. The finished assay is allowed to cool slowly to obviate spitting, and shortly after setting (dropping of the surface) it is removed from the muffle. The beads are removed with sharp-nosed pliers, squeezed, brushed on the under side, and placed on a black wooden board, provided with a number of small holes, ready for weighing on the assay balance.

Assays of upper and lower portions show differences up to three-thousandths in fineness between 980 and 725, and considerably more between 400 and 200.

<sup>1</sup> Cf. Correction Table in *Kerl's Probierbuch*, 3rd edition, p. 106.

<sup>2</sup> Cf. The distinction of silver and imitation silver alloys, p. 122.



If the double assay with 0.5 g. alloy gave a mean weight of 350 mg., which is equivalent to a fineness of 700 per 1000, then, according to the French Coinage and Medallion Commission, a correction of 4.75/1000 should be added for cupellation loss, making the actual assay 704.75 per 1000.

Instead of referring to tables for the correction of cupellation loss, it is more usual to introduce check assays, made up of fine silver, etc., to the approximate amount of the assays, and to add the loss found on these to the assay weights.

This determination of the fineness usually serves as a preliminary only to the much more accurate volumetric estimation by the Gay-Lussac method (cf. *infra*). For low-grade and impure silver alloys of commerce, it is still, however, sometimes used as a definite test.

## B. WET ASSAY FOR SILVER ALLOYS

The two methods which are almost exclusively used for the wet assay of silver alloys are the sodium chloride method of Gay-Lussac<sup>1</sup> and the ammonium thiocyanate method of Volhard.<sup>2</sup> The gravimetric estimation by precipitation of silver chloride, which occupies a longer time than the volumetric method, is seldom used in practice when only the silver content is in question; it is, however, employed in Indian mints,<sup>3</sup> where, owing to the high temperature prevailing and the consequent evaporation of the standard solutions, these cannot be kept at a constant working value.

Electrolytic methods of deposition have not hitherto been introduced, as they do not offer any advantages.

### 1. Gay-Lussac's Sodium Chloride Method.

This method is employed in all mint laboratories. The silver is precipitated, in the cold, from a nitric acid solution of the alloy, which should contain slightly over 1000 mg. of pure silver, by means of a solution of pure sodium chloride (100 c.c. of "standard salt solution"), not quite sufficient to precipitate the whole of the silver; the solution is cleared by shaking, and the silver remaining in solution is precipitated by successive additions of 1 c.c. of a "decimal salt solution," shaking

<sup>1</sup> *Instruction sur l'Essai des Matières d'Argent par la Voie humide*, Paris, 1833; "Vollständiger Unterricht über das Verfahren Gay-Lussacs Silber auf nassem Wege zu probieren," J. von Liebig, 1833; *Die Silberprobiermethode, chemisch untersucht*, by G. J. Mulder, translated from the Dutch by Grimm, 1859.

<sup>2</sup> *Die Silbertitrierung mit Rhodanammonium u. s. w.*, 1878, previously published in the *Berg. u. Hütten. Zeit.*, 1875, 34, 83; 1876, 35, 333 (Lindemann); *J. prakt. Chem.*, 1877 [2], 15, 191.

[L. Campredon, in his *Guide pratique du Chimiste Métallurgiste et de l'Essayeur*, calls this the method of Charpentier, who published the principles of the method in the *Comptes rend.* in 1871.]

<sup>3</sup> For a detailed description, see *The Indian Mint Assay of Silver Bullion*, by F. T. C. Hughes, *Trans. Inst. Min. and Met.*, 1907-8, 17, 334.



well after each addition, until no further turbidity is observable with salt solution.

The solutions required for the determination are:—

1. *Standard Salt Solution.* This is made by dissolving 5.4202 g. of pure sodium chloride in 1 litre of distilled water at 15°.

[If the solution is required for frequent use, it is as well to prepare, say, 50 litres at a time, starting with a cold saturated solution of pure salt, of which 100 c.c., between 10° and 20°, contain 31.84 g. of sodium chloride. A solution of ordinary common salt may be freed from calcium sulphate and magnesium chloride by treating it with barium

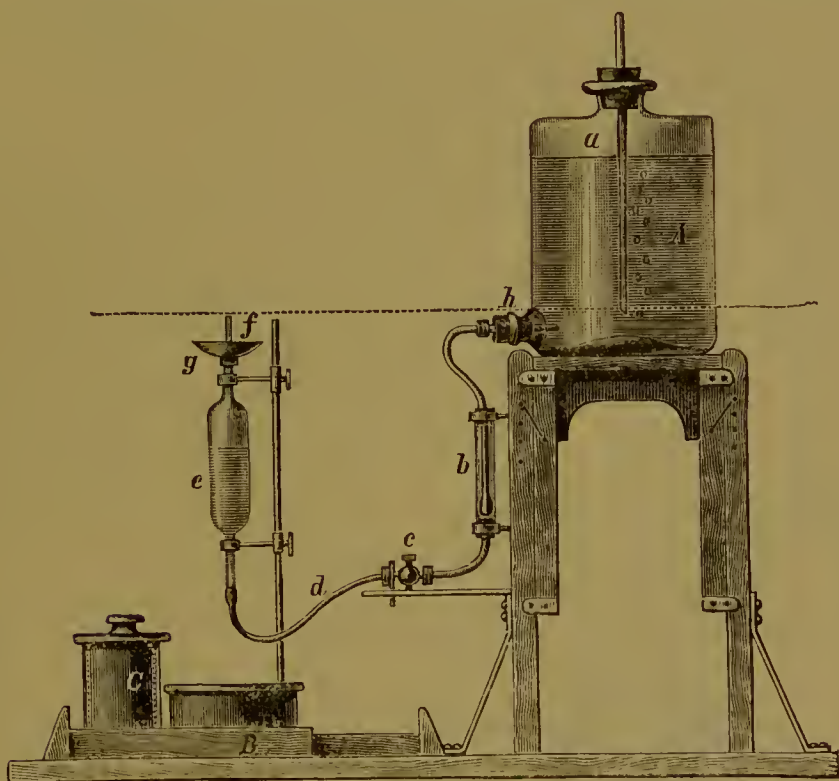


FIG. 43.

chloride and sodium carbonate, filtering, boiling down, and recrystallising the salt thus obtained.]

One hundred c.c. of this solution should precipitate just 1000 mg. of silver; as a little more than this quantity is present in the assay, the completion of the precipitation may be effected with salt solution of one-tenth the strength. From 5 to 10 litres of this standard salt solution are stored in a bottle, supported on a firm wooden stand and provided with a side tubulure near the bottom. The Stas pipette, which has a capacity of exactly 100 c.c., and is a simplification of the Gay-Lussac pipette, is filled from this bottle as shown in Fig. 43.

2. *Decimal Salt Solution*, made by diluting 100 c.c. of solution No. 1 to 1 litre.

3. "*Decimal*" *Silver Solution*. This is made by dissolving 1 g. of chemically pure silver in 6 c.c. of pure nitric acid (sp. gr. 1.2) and diluting to 1 litre.

Both these dilute solutions are kept in glass-stoppered bottles. The approximate silver content of the alloys under examination must be ascertained by a preliminary assay in the dry way, or by Volhard's volumetric method (p. 116).

In the case of mint-prepared alloys (made from silver of known fineness and pure copper), the silver content is already known and merely requires to be checked by the sodium chloride method.

Firstly, the titre, or standard value, of the standard salt solution (which should be at a temperature of as near 15° as possible), is fixed by means of a nitric acid solution of 1.003 g. of chemically pure silver. The silver, in the form of clippings, is treated in a 200 c.c. shaking-bottle with 14 c.c. of pure nitric acid (sp. gr. 1.2), and gently heated in a water-bath until dissolved; when solution is complete, the bottle is placed on a metal guide immediately under the Stas pipette (Fig. 43), which is filled with the standard salt solution (No. 1), and closed at the upper end by means of the finger. In the London mint, a hot-plate covered with asbestos is used in place of a water-bath, and a series of six pipettes is arranged, the filling of which is effected by means of a foot pedal. The solution in the pipette is run into the bottle, which is then closed with its numbered stopper and shaken for five minutes, in such a way that the contents are thrown violently against the sides of the bottle. In doing this, the bottle must be firmly gripped, the forefinger being pressed against the stopper.

The silver chloride clots and settles rapidly; any particles remaining attached to the sides or to the stopper can be detached by sloping and rotating the bottle. After a minute or two, 1 c.c. of the "*decimal*" salt solution (No. 2) is run in from a pipette, the latter being allowed to touch the inner side of the neck of the bottle. If silver still remains in solution, a turbidity is observable near the surface of the liquid when the flask is held to the light, and this spreads through the whole liquid on gently shaking.

The number of cubic centimetres of "*decimal*" salt solution added is marked with chalk on a board, hung up in a convenient position, and divided for the various numbered bottles. The bottle is shaken until clear and the addition of "*decimal*" salt solution continued, 1 c.c. at a time, until no further turbidity is to be seen. The final cubic centimetre, which shows no turbidity, is not counted, and the previous cubic centimetre is counted as a half only, the corresponding chalk-mark being crossed.

As an example, suppose the third addition shows no turbidity, the amount of salt solution used for the complete precipitation of 1003 mg.

of silver = 100 c.c. of "standard" solution is equivalent to 1000 c.c. of "decimal" solution + 1.5 c.c. of "decimal" solution, or altogether 1001.5 c.c. of "decimal" salt solution.

In practice, the thickness of the cloud produced by the addition of the first cubic centimetres is used to indicate the probable amount required.

If an alloy on preliminary dry assay, reckoning also the cupellation loss, shows a fineness of 734/1000, the amount to be taken for the wet assay is arrived at as follows:—

734 mg. Ag are contained in 1000 mg. alloy.  
Then 1003        "        "        "         $x$         "  
 $\therefore x = \frac{1000 \times 1003}{734} = 1366 \text{ mg.}$

Consequently, 1366 mg. are weighed out, dissolved in 10 to 12 c.c. of nitric acid (sp. gr. 1.2), free from chlorine, and the solution treated exactly as described above.

Assuming that the fourth cubic centimetre is the first to show no turbidity, the amount of salt solution =  $1000 + 2.5 = 1002.5$  c.c. of "decimal" salt solution. Since 1001.5 c.c. = 1.003 g. silver, the sample under examination (1366 mg.) contains 1004 mg. silver, which corresponds to a fineness of 735 per 1000.

## Remarks.

1. *Apparatus.* The simple and cheap Stas pipette is a perfectly satisfactory substitute for the original Gay-Lussac pipette. It must be protected against dust, and, if a few drops of the "standard" solution should overflow on to the sides of the pipette, it should be washed with strong sodium hydroxide solution (it must be remembered that 0.1 c.c. of "standard" solution = 1 mg. Ag). In mint laboratories a special stand is used, to allow of several bottles being immersed at the same time in the copper water-bath. For the simultaneous shaking of from ten to twelve samples, a shaking apparatus is provided, having two handles, and suspended from a spring arm, a spiral spring being attached below (Fig. 44). The individual bottles must be fixed by means of wooden wedges, and the glass stoppers must be well secured.

2. *Effect of Foreign Metals, etc.* Black particles, remaining behind

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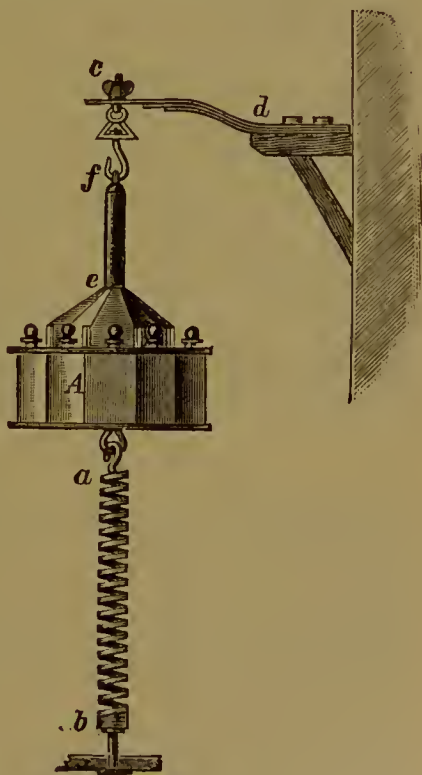


FIG. 44.



on dissolving the alloy, may contain gold, platinum, carbon, or sulphide of silver. The last of these dissolves on continued warming, with addition of 1 to 2 c.c. of strong nitric acid. Turbidity, due to the presence of antimony, disappears on the addition of tartaric acid, which should also be added if bismuth be present. Alloys containing mercury should, according to Debray, be heated gradually in a small graphite crucible in a muffle to the melting point and the button then dissolved in nitric acid.

The presence of lead and tin, according to Kerl, necessitates the use of sulphuric acid as solvent, in place of nitric acid; traces of lead, however, do not interfere.

3. *Action of Silver Chloride.* Investigations by Mulder show that silver chloride is slightly soluble in the sodium nitrate produced during titration, and that, on precipitation of the silver with the calculated quantity of sodium chloride, about 0.5 mg. of silver remains in solution; consequently an excess of 0.5 c.c. of "decimal" salt solution is really used, when the addition of this is continued to the point of complete disappearance of turbidity. This has, however, no influence on the result of the assay, since it occurs to the same extent in standardising with pure silver, as in the assay itself.

4. *Accuracy of the Assay.* The fineness is usually expressed in thousandths; expert assayers can determine the end-point of precipitation, however, to 0.1 mg. by making smaller additions of the "decimal" salt solution than 1 c.c.

Stas (1865) found that the accuracy was about 1 part in 100,000 when the work was carefully done, and has given particulars of how this degree of accuracy was obtained.<sup>1</sup>

Hoitsema<sup>2</sup> has more recently worked with a view of obtaining the highest degree of accuracy, and states that "The accuracy of this determination is of the order  $1/10^6$ —that is, one part in one million." These results were obtained on fine silver.

## 2. Volhard's Ammonium Thiocyanate Method.

This method depends on the precipitation of silver, from nitric acid solution, by means of a solution of ammonium thiocyanate, or potassium thiocyanate, in presence of ferric sulphate as indicator. The curdy precipitate of silver thiocyanate, which is but little affected by light, is insoluble in cold dilute nitric acid; the slightest excess of the precipitant is shown by the persistent red coloration, due to the formation of ferric thiocyanate.

The solutions needed for the determination are :<sup>3</sup>—

1. *Ammonium Thiocyanate Solution.* This salt can be obtained

<sup>1</sup> *Les Lois des Proportions chimiques*, Brussels, 1865, pp. 39-48.

<sup>2</sup> *Dutch Mint Report*, 1903.

<sup>3</sup> Cf. R. Fresenius, *Quantitative Analysis*, 7th edition, vol. ii., pp. 361 *et seq.*; also, E. A. Smith, *Trans. Inst. Min. and Met.*, 1906, 16, 154.



chemically pure and is more suitable than the potassium salt, which frequently contains chlorine. Seven and a half to eight grams are dissolved in water and the solution made up to 1 litre. This is standardised by titrating 50 c.c. of silver solution (No. 2) diluted with 100 to 200 c.c. of water in a beaker, 5 c.c. of a cold saturated solution of iron alum, free from chlorine, being added; the end-point is indicated by a permanent pale brownish red colour. The thiocyanate solution is then diluted so that 1 c.c. is exactly equivalent to 0.01 g. Ag; the value must, of course, be checked by several titrations.

By diluting 100 c.c. of the solution to 1 litre, a "decimal" thiocyanate solution is obtained (1 c.c.=1 mg. Ag); this solution is employed towards the end of the titrations.

2. *Silver Solution.* Ten grams of chemically pure silver are dissolved in 160 c.c. of pure nitric acid of sp. gr. 1.2, in a long-necked flask, care being taken to avoid loss by spitting; the nitrogen oxides are completely driven off, and the solution, after cooling, is diluted to 1 litre. One c.c. of this solution contains exactly 0.01 g. Ag.

3. *Solution of Iron Alum.* A saturated solution free from chlorine is used, of which 5 c.c. are added in each titration. Any yellowish colour in this solution is destroyed by the addition of a little colourless nitric acid.

To carry out the determination, from 0.5 to 1 g. of the sample in the case of alloys is dissolved by means of 10 to 20 c.c. of nitric acid (sp. gr. 1.2), in a beaker covered with a watch-glass, and heated on a sand-bath until nitrous fumes have disappeared. The cover-glass and the sides of the beaker are then washed with water, 100 to 150 c.c. of water and 5 c.c. of the iron alum solution added, and the solution titrated, the beaker being placed on a sheet of white paper.

When the titration approaches completion, the iron coloration disappears only slowly on shaking; the "decimal" thiocyanate solution is then used for finishing the estimation.

Volhard's method gives very good results. In carrying it out, only such measuring flasks, pipettes, and burettes should be used as have been specially checked or calibrated (*cf.* Vol. I., pp. 32 *et seq.*).

*Remarks.*—The solutions must be titrated cold; nitric acid does not interfere, but any nitrous acid must have been previously got rid of by boiling.

The presence of gold in the sample (as, for instance, in crude silver and refined silver) is shown on solution in nitric acid; the dark brown or black powder left as a residue is washed with hot water by decantation, collected into a small crucible, dried, heated, and weighed (*cf.* Assay of Gold, Silver, and Copper Alloys, p. 142).

In the presence of high percentages of copper (above 70 per cent.), the end-point is not sharp, and in such cases an accurately measured

quantity of the silver solution (No. 2) is added to the strongly coloured solution, or a corresponding quantity of pure silver may be added, so that the relation  $\text{Cu} : \text{Ag} = 7 : 3$ , is not exceeded.

Mercury must be previously removed from the alloy by heating.

The presence of palladium causes high silver results to be obtained.

Arsenic, antimony, tin, zinc, cadmium, lead, and bismuth do not interfere with the titration; cobalt and nickel have a similar effect to large quantities of copper, on account of the colour of their nitrate solutions.

A. E. Knorr<sup>1</sup> recommends a combination of the Gay-Lussac and Volhard methods, viz., the precipitation of the greater part of the silver with salt solution, and titration of the remainder with ammonium thiocyanate.

### 3. Gravimetric Estimation of Silver.

The precipitation of silver as chloride has been already mentioned (p. 109). The following gravimetric method, in which the silver (even when present in minute quantities only) is estimated as iodide, is very accurate. Hampe, after careful investigation,<sup>2</sup> strongly recommends the method as described by R. Benedikt and L. Gans<sup>3</sup> for the determination of silver in its alloys with lead. The process is as follows:—

The amount of the alloy to be taken varies from 10 g. to several hundred grams, according to the richness of the lead in silver; it is dissolved in dilute nitric acid, free from chlorine, with addition of tartaric acid should antimony be present. The quantity of nitric acid is so regulated, that there should be an excess of about 10 c.c. The clear solution (filtered if necessary) is considerably diluted (it may be to 300 c.c. or to as much as several litres), and more than sufficient potassium iodide solution, to precipitate the whole of the silver, is added, but too great an excess should be avoided; the containing vessel is then covered and heated. The lead iodide dissolves, and reacts with the nitric acid, and iodine is set free. Heating is continued until the iodine is volatilised and the liquid appears colourless. The silver iodide is filtered off and weighed; or it can also be converted into chloride and weighed as such.

Benedikt examined poor leads, the silver contents of which were very carefully ascertained in the dry way to be 0.003 per cent. and 0.0006 per cent. respectively. By his method, using 147 g. and 239 g. of material respectively, he found 0.0034 and 0.00054 per cent. of silver.

Hampe checked the method by precipitation of minute quantities of silver, in presence of considerable amounts of chemically pure lead nitrate (320 g. of lead nitrate, 1 mg. of silver as silver nitrate, 2 litres of

<sup>1</sup> *J. Amer. Chem. Soc.*, 1897, **19**, 814.

<sup>2</sup> *Chem. Zeit.*, 1894, **18**, 1899; *J. Soc. Chem. Ind.*, 1895, **14**, 304.

<sup>3</sup> *Chem. Zeit.*, 1892, **16**, 4, 12.

water, and 10 c.c. of nitric acid, precipitation being effected by 0.5 g. of potassium iodide in aqueous solution). The result obtained was 0.98 mg., instead of 1 mg.

The method is especially suitable for the examination of assay lead, litharge, and red lead, which are intended for dry assay work.

**The Examination of Bar Silver** (Crude and Refined Silver, Fine Silver, Cement Silver).—A complete analysis is seldom required. It is usual to determine the gold left on dissolving a fairly large quantity of the sample (10 g. or more) in pure nitric acid (*cf.* Gold, p. 143), then the silver in an aliquot part of the solution, either by the Gay-Lussac or Volhard method, or gravimetrically, and finally an examination is made for impurities, more particularly bismuth, a small amount of which has the effect of producing brittleness and hardness in silver alloys (*e.g.*, coinage alloys).

The presence of antimony and tin may be recognised by qualitative tests, a few grams of the alloy, dissolved in pure nitric acid, showing, in this case, a whitish turbidity; copper gives a blue coloration with excess of ammonia, and lead and bismuth are at the same time precipitated as hydroxides.

Platinum and the platinum metals are almost always present, but usually only in traces. H. Rössler has frequently found palladium in refined silver; weighable quantities colour the nitrate solution yellowish.

Sulphur is determined by heating a considerable quantity of the sample, in the form of drillings, in a current of chlorine. This is conveniently effected in a long porcelain boat, placed in a hard-glass tube. The volatile chlorides are collected in a receiver, containing water acidified with hydrochloric acid, and the sulphur is precipitated as barium sulphate. In this way also bismuth, tin, arsenic, and antimony can be separated from silver, by the volatilisation of their chlorides; copper, lead, and iron remain in part with the silver chloride and partially in the cooler portions of the glass tube beyond the boat.

H. Rössler and H. Debray have found selenium in silver. According to Debray it may be determined as follows:—About 100 g. of the silver are dissolved in nitric acid (sp. gr. 1.3), the gold removed by decantation, the silver precipitated with hydrochloric acid, and the filtrate evaporated to dryness. To convert the selenic acid to selenious acid, the residue is boiled with hydrochloric continuously for a quarter of an hour, and the selenium precipitated, as a red powder, by means of a solution of sulphurous acid. The precipitate is transferred to a weighed filter paper, washed well with water, the filter paper and its contents dried for from three to four hours in an air-bath at 100°, and weighed.

**Estimation of Silver in Plating Solutions (Silver-baths).**—Silver-



baths usually contain, per litre, from 4 to 20 g. of silver, as silver-potassium cyanide, and from 10 to 50 g. of potassium cyanide, and, in addition, potassium cyanate and potassium chloride, with a little copper, zinc, and nickel as impurities. Cadmium is now frequently added to these baths as cadmium potassium cyanide, since the plating produced tarnishes less readily than a pure silver deposit.

For the analysis, 10 c.c. of the solution are placed in a covered porcelain dish, 10 c.c. of hydrochloric acid added, and the whole heated on a water-bath in a fume cupboard for fifteen minutes; the cover-glass is then removed and washed, and the contents of the dish evaporated to dryness on the water-bath. The presence of a small quantity of copper is indicated by a brownish colouring of the residue, due to anhydrous chloride of copper. The dry mass may either be treated by scorification followed by cupellation, or digested with 25 c.c. of water and a few drops of nitric acid, the residue filtered off after cooling, washed with water containing nitric acid, dried in an air-bath, incinerated in a Rose's crucible, whereby a considerable amount of silver chloride is reduced, then strongly heated for five to ten minutes in a current of hydrogen or coal gas, and any carbon subsequently burnt off.

Any copper contained in the filtrate from the silver chloride, which usually amounts to a few milligrams, may be precipitated with sulphuretted hydrogen, the precipitate collected on a small filter paper, washed with water containing a drop of sulphuric acid and a few cubic centimetres of sulphuretted hydrogen solution, dried, and roasted in a porcelain crucible (finally over a large Bunsen flame) to cupric oxide:  $\text{CuO} \times 0.7989 = \text{Cu}$ .

If cadmium be present, both metals are precipitated as sulphides; in this case the washed precipitate is washed off the filter paper into a porcelain dish and boiled for five to ten minutes with dilute sulphuric acid (1:5), whereby the cadmium sulphide is completely dissolved (A. W. Hofmann's method). The sulphide of copper is treated as described. The cadmium is precipitated again, from the largely diluted solution, as sulphide, collected on a tared filter, dried at  $100^\circ$ , and weighed, after being allowed to cool for half an hour.  $\text{CdS} \times 0.7780 = \text{Cd}$  (*cf.* Cadmium, p. 303).

The potassium cyanide content of baths is most rapidly determined by titration with silver nitrate solution (*cf.* Vol. I., p. 550).

**Recovery of Silver from Silver Chloride and Silver Thiocyanate.**—Chloride of silver is boiled repeatedly with dilute hydrochloric acid, washed thoroughly with water by decantation, and dried; it is then mixed with half its weight of anhydrous sodium carbonate and one-eighth its weight of potassium nitrate, and the mixture gradually introduced into a roomy clay crucible, placed in a wind-furnace, and



heated until the melt is tranquil; the slag is poured off and the metal cast in a warm ingot mould, or granulated by pouring in a thin stream into water, which is kept in agitation. The ingots are cleaned with hot, dilute sulphuric acid.

At the Paris mint one hundred parts of silver chloride are run down with seventy parts of chalk and four parts of powdered wood charcoal.<sup>1</sup>

Reduction of silver chloride may also be effected by treatment with water and pieces of pure zinc and a little sulphuric acid; the spongy silver obtained is treated with hot, dilute sulphuric acid to dissolve the zinc, washed well with water, dried, and melted down with nitre and borax.

Pfeiffer<sup>2</sup> prepares pure silver by the electrolytic decomposition of silver chloride in a porous porcelain cell, as follows:—A strip of platinum foil or a rod of iron is surrounded, in a porous cell, by well-washed silver chloride, moistened with dilute sulphuric acid; a thick amalgamated zinc cylinder is placed outside the cell, and the whole inside a glass battery jar containing dilute sulphuric acid. The zinc and platinum poles are then connected up. After reduction, the spongy silver is repeatedly washed, and then either melted down or worked up directly to silver nitrate.

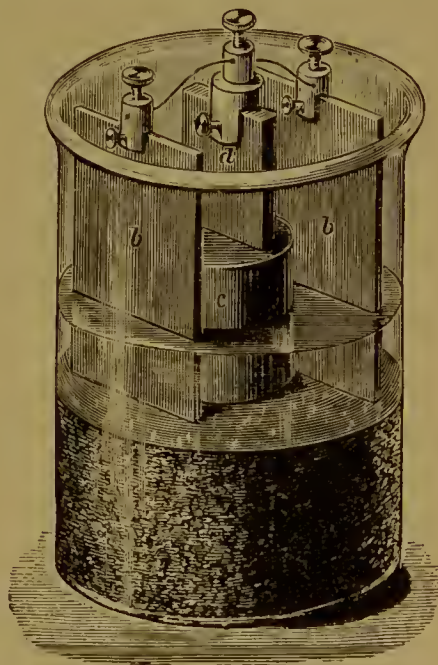


FIG. 45.

An almost identical method has been described by Priwoznik.<sup>3</sup> Instead of the platinum used by Pfeiffer, two silver strips are employed. Water slightly acidified with sulphuric acid is poured into a porous cell, 27 cm. in height and 8.5 cm. wide (*c*, Fig. 45), and two heavy zinc rods, or a thick zinc plate, *a*, are introduced and connected by copper wire with two silver strips, *b*, each 12 cm. wide. These latter stand in silver chloride moistened with sulphuric acid (1:10), contained in a glass jar 32 cm. high and 22 cm. in diameter. The porous cell also stands in the silver chloride. The amount of silver chloride contained in the jar corresponds to about one kilogram of silver. The zinc plates require frequent cleaning.

Pure silver (assay silver) is prepared electrolytically in this way, in

<sup>1</sup> Kerl, *Metallurgische Probierkunst*, 2nd edition.

<sup>2</sup> *Chem. Zeit.*, 1898, 22, 775; *J. Chem. Soc. Abstr.*, 1899, 76, 366.

<sup>3</sup> *Oesterr. Zeitschrift f. Berg. u. Hüttenwesen*, 1879, 418; Balling, *Fortschritte im Probierwesen*, 1887, pp. 18, 19.

the mints at Vienna, Sydney, Melbourne, etc., from the silver nitrate solution obtained in gold parting by inquartation.

To obtain silver chloride from silver thiocyanate, von Juptner recommends boiling it with three to five times its volume of hydrochloric acid, nitric acid being added, drop by drop, until the red coloration at first produced disappears. The silver chloride is then washed, dried, and treated as described above.

**The Distinction of Silver from Imitation Silver Alloys.**—According to Rössler, the streak on the touchstone is tested by treating it with a drop of nitric acid and adding a minute quantity of hydrochloric acid to the solution so obtained (*cf.* p. 111).

Imitation alloys, base coins, etc., are cleaned with soap and rubbed on a moistened spot with a stick of silver nitrate; a heavy black stain is at once noticeable in the case of base metals. This is the method frequently employed in banks.

Silver and silver-plated goods, when treated with a cold saturated solution of potassium bichromate in nitric acid of sp. gr. 1.2, immediately show a cherry-red stain of silver chromate, which does not wash off. Should there be a suspicion that the goods are plated, the upper layer is removed on one part, and the bared metal, which frequently is of a different colour, is treated with bichromate solution. The red stain is not produced on German silver, brass, tombac, etc.

Thin plating may be recognised, according to R. Finkener, as follows:—The article to be tested is cleaned with alcohol and ether, to remove lacquer, and then treated with a 1.5 per cent. solution of yellow sodium sulphide, obtained by boiling a solution of 30 g. of crystallised sodium sulphide in 10 c.c. of water for ten minutes with 4.2 g. of flowers of sulphur, and diluting to a litre. After contact with this solution for ten minutes, the article is washed with water.

Silver shows an even steel-grey stain; imitation alloys, at best, show a ring darkened at the edges.

As amalgamated copper, which, however, is seldom met with, behaves in much the same way as silver under this treatment, it is well to heat the article first and so remove any mercury which might be present.

## GOLD

Native gold, all gold ores and commercial products, most gold alloys and sweep from these, usually contain silver in varying amounts. As a rule, therefore, in the assay of these materials, the gold and silver are obtained as an alloy, which is then subjected to the operation of parting.

The dry assay of ores, etc., is, with few exceptions, identical with the dry silver assay: viz., scorification, or pot assay, followed by

cupellation of the lead button. In some cases the wet and dry methods are combined.

The high value of gold, and the corresponding effect of differences in the assays, render especial care necessary in taking representative samples. This is somewhat complicated by the fact that the gold mostly exists in ores as native gold and is very unevenly distributed. The same holds good for gold sweep from alloys, which often have to be assayed. Further, ingots of gold alloys are not entirely uniform throughout.

### Gold Ores.

The most important sources of gold are :—

*Native Gold*, with 0.16 to 38 per cent. silver (Electrum), usually also some copper and iron.

*Gold Amalgam* and *Gold-Silver Amalgam*, containing respectively up to 39.5 per cent. gold and 36 per cent. gold, with 5 per cent. silver.

*Palladium Gold*, with 86 per cent. gold, 4.1 per cent. silver, and 9.8 per cent. palladium.

*Rhodium Gold*, with 57 to 66 per cent. gold and 34 to 43 per cent. rhodium.

*Bismuth Gold*, with 64.5 per cent. gold.

Very frequently gold ores contain *Tellurium*; such ores are found more particularly in the Siebenbürgen, in Colorado and in Western Australia.

The following minerals may also be mentioned :—

*Petzite* ( $x \text{ Ag}_2\text{Te} + \text{Au}_2\text{Te}$ ), containing 3.3 to 25.6 per cent. gold and 40.8 to 46.8 per cent. silver.

*Sylvanite*, *Calaverite* ( $x \text{ AuTe}_2 + \text{AgTe}_2$ ), containing 26.5 to 40.6 per cent. gold and 2.24 to 11.3 per cent. silver.

*White Tellurium*, or *Krennerite*, containing 24.9 to 29.6 per cent. gold, 2.7 to 14.6 per cent. silver, and 2.5 to 19.5 per cent. lead.

*Foliated Tellurium*, or *Black Tellurium* (*Nagyagite*), containing 5.9 to 7.6 per cent. gold, and 57.2 to 60.5 per cent. lead.

*Tellurium Silver* (*Hessite*),  $\text{Ag}_2\text{Te}$ , often contains gold.

Small quantities of gold are contained in iron pyrites, copper pyrites, arsenical pyrites, mispickel, etc.; for instance, copper ores from Rammelsberg were found to contain one part of gold in two million and copper pyrites from Fahlun one part in a million.

## I.—METHODS OF ORE ASSAY

### 1. Dry Assays.

As the method to be employed in the dry assay of gold depends largely on the character of the ore, it is advisable to carry out a preliminary examination by mechanical and chemical means.



Simple washing methods are particularly valuable for this preliminary examination. The apparatus used consists of either a wooden pan (Figs. 46 and 47), or an iron or wooden dish called the Batea (Fig. 48), or of flat porcelain dishes or plates.

The material, in a fine state of division, is shaken with water on the pan (Fig. 46), and the muddy water carefully poured off, so that the residue forms a thin mud. The pan is then held horizontally, gentle end taps are given to it, and at the same time it is moved sideways, the action being similar to that in mechanical concentrators. After a short time the different constituents of the ore separate according to their specific gravities. Porcelain dishes are manipulated in much the same way. By rejecting the apparently non-metallic products, adding fresh material and repeating the operations, an enrichment of the specifically heavy products is ultimately attained. A zone of more or less finely-divided gold cannot always be detected with certainty, for some ores, as, for instance, the Transvaal conglomerates, contain most of the gold in

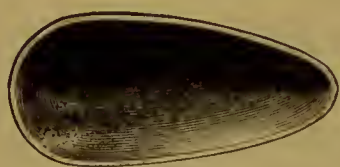


FIG. 46.



FIG. 47.

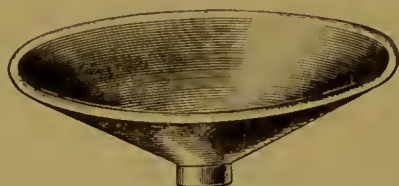


FIG. 48.

an extremely fine state of division, in tiny microscopic leaflets, and much of this passes off with the finest of the mud in the process of washing.

Other accompanying minerals, such as pyrites, etc., are, however, easily visible, and small quantities of these can be then examined before the blowpipe. Tellurium-gold and tellurides (see above) must be carefully looked for; these may easily be mistaken, when in a finely-divided state, for mispickel or arsenical pyrites. The tellurides, on gently warming with 1 c.c. of concentrated sulphuric acid in a test tube, give a cherry-red solution; the colour disappears on heating more strongly.

A more delicate test consists in heating the ore with nitric acid, diluting somewhat, filtering, evaporating the filtrate with sulphuric acid until dense fumes are evolved, and then adding tin foil. The same carmine colour is produced. In both these tests the presence of iron interferes with and often completely masks the colour due to tellurium.

An excellent test consists in heating the ore in a current of chlorine,<sup>1</sup> the ore being contained in a glass tube, the end of which is bent and

<sup>1</sup> Holloway and Pearce, *Trans. Inst. Min. and Met.*, 1907-8, 17, 171.



made to dip into hydrochloric acid. The heat required is below dull redness, and the chlorine should be passed for about one hour. The hydrochloric acid solution thus obtained is diluted, nearly neutralised with sodium carbonate or ammonia, and saturated, whilst still warm, with sulphur dioxide. The tellurium often takes some hours for complete precipitation, and the solution should, therefore, be left in a warm place over night.

The distillation in chlorine may be obviated by fusing the ore with sodium peroxide in a nickel, iron, or copper crucible, boiling with water, filtering, neutralising with hydrochloric acid, and passing in sulphur dioxide as above. Either of these methods results in the precipitation of selenium, as well as tellurium; the former, however, is soluble in potassium cyanide solution, and may thus be separated and reprecipitated as a red powder by acidifying the solution with hydrochloric acid and heating. For a quantitative determination of tellurium in an ore, the chlorine distillation method may be recommended.

When the Batea (Fig. 48) is used for the preliminary treatment of the ore, the specifically lighter portions of the powdered ore are removed by a circular and sloping motion; the heavier particles form a tail on the lower portion of the pan.

(a) **Scorification Assay.**—The silver scorification assay (pp. 98 *et seq.*), as stated above, also holds, as a rule, for gold. The process is particularly applicable to rich gold ores not containing tellurium, to all ores containing lead and those rich in copper, to furnace products, and to sweep<sup>1</sup> free from carbonaceous material.

In regard to the quantities of assay lead and borax required, see p. 99.

In carrying out the scorification assay, it is very frequently necessary to “concentrate,” *i.e.*, the lead buttons from a number of scorifications are united and scorified together, and so on, until finally, on cupellation, a sufficiently large bead of silver and gold is obtained.

(b) **Pot Assay** (*cf.* Silver, pp. 101 *et seq.*).—This process is eminently suited to many auriferous materials, and is largely used in England and in the United States, Mexico, and South America; it allows of larger amounts of ore being taken (up to several hundred grams), and consequently the effect of an uneven distribution of the gold on the assay is decreased.

The fusion is effected in smooth-walled crucibles, either in an ordinary wind-furnace or in a gas- or oil-furnace. Details as to charges for simple ores (flux, reducing material, litharge, red lead, etc.) are given in the section on the Silver Assay (pp. 103 *et seq.*).

Weill<sup>2</sup> states that in America the pot assay is frequently performed in muffle furnaces, whereby a more uniform heating of the crucibles is

<sup>1</sup> *Cf.* A. Görz, *Berg. u. Hütten. Zeit.*, 1886, 45, 441.

<sup>2</sup> *L'Or*, by L. Weill, 1896.

attained. From six to eight crucibles are put into the muffle at one time, the ore charge being from 20 to 100 g.

According to Mitchell, the quantity of ore to be taken, in the case of rich material containing 5 to 10 oz. of gold per American ton (2000 lb. avoirdupois), is 1 assay ton (29.166 g.); in the case of poor material, 2 to 4 assay tons, and for very rich ores, half an assay ton.

A satisfactory charge is:—For 1 assay ton of ore, 1 assay ton of sodium carbonate, 1 of red lead, 0.25 of fused borax, and 0.05 of charcoal. The fusion is carried out in a wind-furnace, the temperature being gradually increased by regulating the damper; towards the end a strong heat is employed. The crucible, on being taken from the furnace, is gently tapped on the furnace plate and allowed to cool, or, preferably, the contents may be poured at once into a warm iron mould (Fig. 40, p. 104); in the latter case one crucible will serve for five or six fusions.

The slag from the fusion of very rich ores is run down with 25 to 30 g. of red lead, 1 to 2 g. of charcoal powder, and a little sodium carbonate, and the resulting lead button cupelled.

Ores containing much sulphur, arsenic, or antimony, are subjected to a preliminary roasting, first alone, and finally, after admixture with a little charcoal powder, in fire-clay roasting dishes or sheet iron trays, washed over with fire-clay or ruddle. To prevent loss of gold, the temperature must be raised very gradually. W. Witter has proved that pyritic ores roasted with this precaution suffer no loss of gold; he has also pointed out that ores containing small quantities of tellurium or mercury must undergo a more protracted roasting at a low temperature before heating more strongly.

For the assay of mint sweep, etc., the following method will be found to be very satisfactory. A sample of 500 g. is taken, and the moisture first determined. The dried sample is then passed through an eighty-mesh sieve, and the metallic particles are collected, weighed, and assayed separately. Of the fine material, 25 g. are thoroughly roasted and mixed with 60 g. of red lead, 1.5 g. of charcoal, 30 g. of sodium carbonate, and 30 g. of borax, and run down in a pot in the usual way. The button of lead obtained should weigh about 30 g.; if the material be rich, the slag is re-melted, and a mixture of 20 g. of red lead and 1 g. of charcoal added; a second lead button is thus obtained. The lead buttons are then cupelled and parted in the usual way (Bannister).

In smelting roasted pyrites, a sufficiency of charcoal powder must be used, so that the ferric oxide may be reduced to ferrous oxide, and the latter must be slagged off by means of a sufficient amount of borax or powdered glass. If too little charcoal powder be used, reduction of the lead from the red lead or litharge used is not effected.

When the melt has become tranquil, a little red lead, mixed with charcoal and flux is thrown in, to carry down any prills suspended in the slag. Witter states that it is not advisable to assay more than 200 g. of material in one melt, otherwise lower yields are obtained than if a number of melts of 100 g. each are carried out.

The methods to be used in the assay of complex gold ores vary with the nature of the associated minerals. General instructions for their treatment have been given by E. A. Smith.<sup>1</sup>

Arsenical ores, as already stated, require a preliminary roast to get rid of the arsenic. For their assay, 1 assay ton of ore is placed on a roasting dish in a cool muffle, and roasted carefully at a low temperature at first, stirred frequently, and the temperature gradually raised. When no incandescent particles are visible, the temperature is raised to full redness. After a time 5 to 10 per cent. of powdered anthracite is mixed in, and the whole again roasted at a full red heat.

When there is no further smell of arsenic or of sulphur, the roast is mixed with the following charge and fused down in the usual way:—red lead 1, charcoal 0.1, sodium carbonate 0.75, borax 0.25, assay tons.

Antimonial ores<sup>2</sup> are best treated by a fusion method in which sufficient nitre is added to the charge to partially oxidise the stibnite, the remainder being oxidised by the red lead, which at the same time forms a lead button to carry down the precious metals. The amount of nitre necessary must be determined by experiment, the object being to obtain a soft lead button weighing about 30 g. The following is a useful charge for average ores:—

	Assay Tons.
Ore . . . . .	1.0
Red lead . . . . .	2.0
Sodium carbonate . . . . .	0.75
Borax . . . . .	0.2
Nitre . . . . .	0.5 to 0.75

If the resulting button be hard, it should be scorified with the addition of assay lead before being cupelled.

Telluride ores<sup>3</sup> are best treated by crucible assay in which an excess of red lead is used. A moderately hot fire is required for the fusion, but great care is necessary to avoid excessive heating at the commencement. Owing to the corrosive action of litharge on the crucibles used, an addition of burnt fire-clay to the charge is found to be most useful, and is preferable to sand.

The following is a useful average charge for telluride ores. The amount of red lead required varies with the amount of tellurium

<sup>1</sup> "The Assaying of Complex Gold Ores," *Trans. Inst. Min. and Met.*, 1901-2, 9, 315.

<sup>2</sup> Kitto, *ibid.*, 1906-7, 16, 89.

<sup>3</sup> Holloway and Pearce, *ibid.*, 1907-8, 17, 171; *cf.* also, S. W. Smith, *ibid.*, p. 463.



present, the more tellurium the greater must be the excess of red lead used :—

	Assay Tons.
Ore . . . . .	1.0
Red lead . . . . .	1.0 to 4.0
Charcoal . . . . .	0.05
Sodium carbonate . . . . .	1.0
Borax . . . . .	0.5
Burnt fire-clay . . . . .	0.5

Large buttons from this fusion may be scorified before being cupelled, but in this case the operation must not be carried sufficiently far to cause the lead to become covered with slag, as under these conditions tellurium is found to pass again from the slag into the lead button.

Auriferous tinstone<sup>1</sup> should be assayed by the crucible method; an excess of red lead and sodium carbonate is desirable. The following charge will be found to give good results, even with dressed tin ores carrying gold :—

	Assay Tons.
Ore . . . . .	1.0
Red lead . . . . .	2.0
Charcoal . . . . .	0.05
Sodium carbonate . . . . .	1.5
Borax . . . . .	0.25

(c) **The Cupellation of the Auriferous Lead** (*cf.* Silver, pp. 105 *et seq.*).—Lead buttons from the pot assay, when the slag is difficult to remove, are re-melted for a short time on scorifiers; the slag is then easily removable, and the buttons are then brushed. Hard, impure lead buttons are scorified with assay lead before cupellation.

Towards the end of the cupellation of auriferous lead, the temperature should be raised, as is the case in the silver assay. Beads rich in gold do not “spit.”

There is a distinct loss of gold by absorption during cupellation. To recover the gold from the cupels, the portions not saturated with litharge are removed, and the rest is treated as follows :—One hundred parts of cupel substance are melted in a crucible with seventy-five parts of fluor spar, seventy-five of sand, one hundred of sodium carbonate, fifty of borax, and two of powdered charcoal. The lead button obtained is then cupelled.

(d) **Parting**.—After having been weighed on an assay balance, the beads are parted by means of nitric acid or concentrated sulphuric acid. Complete separation is only attained if the ratio of gold to silver is 1 : 2.5 or 1 : 3 and above (*cf.* p. 134).

Alloys of forty parts gold and sixty parts silver are so white that

<sup>1</sup> Bannister, *Trans. Inst. Min. and Met.*, 1905-6, 15, 513.



they cannot be distinguished in appearance from silver; an alloy of seventy parts gold and thirty parts silver has a pale brass-yellow colour.

To effect the "parting," a white bead is flattened out on a polished anvil and treated in a test tube or small porcelain dish or crucible with a few cubic centimetres of pure nitric acid (sp. gr. 1.2 to 1.3), free from chlorine, the dish covered with a watch-glass, and the contents heated to boiling. If the button disintegrates and the gold separates as a black powder, more silver is present than is actually necessary for the parting. Boiling is continued so long as coloured nitrous fumes are given off; the acid is then carefully poured off, the residue is washed repeatedly by decantation with distilled water, and the gold dried, either on the water-bath or in an air-bath, and finally heated gradually to redness. The black powder turns yellow and becomes somewhat coherent. After cooling, it is brushed on to the balance pan and weighed. The silver is ascertained by difference.

A white bead, that turns brown and is only attacked on the surface by nitric acid, does not contain sufficient silver for parting. Such a bead must be washed, dried by heating, wrapped in lead foil with two or three times its weight of assay silver in small pieces, and the whole placed on a heated cupel and cupelled, an operation which takes only a few minutes to perform; yellow or yellowish beads are treated similarly, without first testing with nitric acid.

Direct melting of the bead with the inquartation silver is simpler; this is done in a hole in a piece of charcoal or on a cupel before the blowpipe. The flattened bead is parted with nitric acid as explained. If the parting is effected with concentrated sulphuric acid, whereby a denser yellow residue of gold is obtained, a second boiling with dilute sulphuric acid is necessary, on account of the sparing solubility of silver sulphate; in this case, however, platinum and traces of lead remain with the gold, whereas small quantities of platinum are dissolved from the alloy, if nitric acid be used in the parting. The solubility of silver-platinum alloys is given on p. 141.

When the relation of gold to silver in the bead is 1 : 2.5 or 1 : 3, boiling twice with nitric acid is sufficient for complete parting, and the bead retains its original shape. Of course the exceedingly porous nature of the gold lowers its cohesive character, but there is the great advantage that less loss occurs on boiling, washing, and collecting, than when the gold is in a finely divided condition.

Plattner's blowpipe assay for gold<sup>1</sup> is of especial use to prospectors. It consists of a crucible assay or scorification assay, concentration, and cupellation. Since only small quantities of material can be used (100 mg. for each assay), the material is, as far as possible, previously enriched

<sup>1</sup> Cf. *Manual of Qualitative and Quantitative Analysis with the Blowpipe*, Plattner; English translation by N. B. Cornwall, 1902.

by panning (*cf.* p. 124). The tiny gold beads are measured with a scale.

G. Koenig's process<sup>1</sup> is an outcome of the Plattner methods, and gives good results. A small muffle furnace, heated with a Hoskins gasoline burner, serves for crucible melts, scorifications, and cupellations; the author states that the work can be carried out from four to six times as quickly as in an ordinary muffle, and that the losses by cupel absorption are not greater than is usually the case.

## 2. Combined Wet and Dry Assays for Ores.

**Plattner's Chlorination Method.**—Poor quartzitic material and pyritic ores, roasted "sweet," are slightly moistened and treated with chlorine, free from hydrochloric acid, for about an hour, in quantities up to 500 g. The treatment is carried out in a tall glass cylinder with a side tubulure. The soluble gold chloride is washed out with hot water, and any free chlorine boiled off. The gold is then precipitated with ferrous sulphate, in presence of a little hydrochloric acid, and is collected on a filter, which, after drying, is incinerated in a porcelain crucible. The gold and filter ash are melted with 5 g. of assay lead on a scorifier, and the button thus obtained is cupelled.

The lower portion of the glass cylinder is packed with pieces of quartz or broken porcelain or similar material; above this, powdered quartz is placed to serve as a filtering medium, and the moistened ore, which should not be tightly packed, is placed on the top. A slow current of washed chlorine is passed upwards through the side opening for an hour.

Silver contained in the ore is converted into chloride, and this, owing to its coating the gold particles, prevents the complete action of the chlorine on the gold. In working with argentiferous ores from the Siebenbürgen, C. Balling<sup>2</sup> was able to extract only 92 per cent. of the actual gold present, in spite of repeated treatment with hot salt solution and chlorine gas. Pufahl obtained better results from similar ores, by the combination of wet and dry methods for silver ores containing gold. Otherwise, the Plattner method gives excellent results.

**Other Gold Extraction Methods.**—In order to ascertain the most satisfactory method for working on the large scale, R. Goering<sup>3</sup> moistens 100 to 150 g. of roasted powdered ore with water, and treats this in a stoppered bottle with from 7 to 35 g. of fresh bleaching powder, and 30 to 150 c.c. of hydrochloric acid, or with saturated

<sup>1</sup> *Berg. u. Hütten. Zeit.*, 1898, 57, 335. Two drawings of the furnace are given in the paper.

<sup>2</sup> *Probierkunde*, 1879, p. 347.

<sup>3</sup> Private Communication from R. Goering, Homestake Assay Office, Dakota, January 1890, to Prof. Pufahl.

bromine water; the bottle is wrapped in a thick cloth and repeatedly shaken; after standing over-night, the solution is filtered, and the gold, both in solution and in the residue, determined by the usual methods. The estimations are carried out simultaneously, both with roasted and unroasted ores of various degrees of coarseness.

Extraction with aqueous potassium cyanide is investigated similarly. The ore is treated with 1 per cent. or more dilute solutions of potassium cyanide, for varying lengths of time, the solution filtered, mixed with pure litharge, evaporated to dryness on the water-bath, and then run down with the usual fluxes in a crucible, and the lead button cupelled. Evaporation to dryness of the auriferous cyanide solution in a small lead dish, followed by scorification and cupellation, may also be adopted. The residues from the cyanide extraction are also assayed for gold.

For the determination of gold in cyanide solutions produced on a large scale,<sup>1</sup> the following method has been found satisfactory. Two hundred and fifty cubic centimetres of the solution are placed in a beaker, 4 g. of zinc shavings and 30 c.c. of 20 per cent. lead acetate solution added, and the whole boiled for one minute; 30 c.c. of concentrated hydrochloric acid are then added to dissolve the zinc, and when all action has ceased, the solution is boiled and allowed to stand until cool. The clear liquor is decanted, the residual spongy lead collected, squeezed into a ball, wrapped in lead foil, dried, cupelled with a little silver, and parted in the usual way.

**The Detection of Minute Quantities of Gold.**—The roasted ore is shaken with an alcoholic solution of iodine; the solution is then absorbed by a few strips of Swedish filter paper, and, after drying and incinerating these, the presence of gold is indicated by the purple colour of the ash (Skey).

A delicate reaction consists in treatment with bromine water, concentration of the solution by evaporation, and addition of stannous chloride, whereby a precipitate of purple of Cassius is produced.

Carnot's colorimetric gold assay<sup>2</sup> depends on the production of a rose to purple tint in a hydrochloric acid solution containing gold, by the addition of zinc dust, in the presence of arsenic acid and ferrous chloride. Solutions are used containing gold varying from 1 mg. per 100 c.c. to 1 mg. per 1000 c.c. Details of this method and of Rose's colorimetric stannous chloride method are given in T. K. Rose's textbook on *The Metallurgy of Gold*.<sup>3</sup>

<sup>1</sup> For the methods of examination of cyanide solutions from gold cyaniding works, cf. *The Chemistry of Cyanide Solutions*, by J. E. Clennell, 1904.

<sup>2</sup> Cf. Weill, *L'Or*, 1896, p. 378; *Berg. u. Hütten. Zeit.*, 1896, 55, 215; *J. Soc. Chem. Ind.*, 1896, 15, 674.

<sup>3</sup> *The Metallurgy of Gold*, by T. Kirke Rose, 5th edition, 1906, pp. 27, 468; cf. also, *Chem. News*, 1892, 66, 271.



V. Schmelck<sup>1</sup> also makes use of the action of stannous chloride on gold solutions, for colorimetrically determining minute quantities of gold.

Mayençon<sup>2</sup> states that a very delicate method of detection consists in electrolytically depositing the gold on a platinum wire.

T. Döring<sup>3</sup> recommends the following method for the detection of small quantities of gold in ores:—One hundred grams of the finely powdered ore are slightly but evenly moistened in a stoppered bottle with 1 to 2 c.c. of a mixture of about equal volumes of bromine and ether, by shaking the ore for at least a couple of hours in contact with the solvent. During this time the interior of the bottle must appear well filled with bromine vapour. Subsequently, 50 c.c. of water are added, and digestion is allowed to take place for a couple of hours, with occasional shaking. The whole is then filtered, and the clear solution evaporated to about one-fifth its volume; a little bromine water is added, to allow of the subsequent formation of a little stannic chloride, which is necessary for the production of the purple tint, and then the solution is treated with stannous chloride in a narrow test tube, and the colour observed. A 0.1 per cent. gold solution shows at once a deep brownish violet coloration, which is opaque, even in thin layers. In a solution containing 0.01 per cent. of gold, an immediate brownish violet colour is produced, and a 14 cm. deep column is opaque. With 0.001 per cent. of gold, an immediate pale violet tint results, which increases in depth after a few minutes; a 14 cm. column is transparent. With 0.0005 per cent. of gold, the stannous chloride shows, after several minutes, especially in thicker layers, a pale violet-red colour, which gradually becomes more intense. Solutions containing 0.0001 per cent. of gold require to be first evaporated to about one-fifth of their volume; a drop of bromine water is then added, after which the addition of stannous chloride will show a distinct rose tint in a 14 cm. column. Solutions containing 0.00005 per cent. of gold, treated similarly, show a very faint but still recognisable rose tint in a column 14 cm. deep. In the case of the very weak solutions, the colorations can be detected with greater certainty, if compared with a 14 cm. column of pure water in a test tube. The method, as described, is applicable to (a) pure quartzose ores; (b) impure quartz, especially if containing iron; (c) pyritic ores, even when containing antimony and arsenic; when notable quantities of sulphur, antimony, or arsenic are present, the ore should be roasted previous to extraction; (d) good results can be obtained with ores containing sulphides of other heavy metals, for instance with galena, zinc blende, and copper pyrites; but in such cases the ore should be subjected to a preliminary roasting. In the case of ores containing

<sup>1</sup> *Chem. Zeit.*, 1898, 22, 271.

<sup>2</sup> *Berg. u. Hütten. Zeit.*, 1887, 46, 403.

<sup>3</sup> *Ibid.*, 1900, 59, 49, 73, 97.



copper pyrites, a certain amount of cupric bromide goes into solution during extraction, and then, on subsequent addition of stannous chloride, a white crystalline precipitate of cuprous bromide is produced; on account of its white colour, however, this does not interfere to any extent with the observation of the purple coloration. The method is not applicable with any certainty to ores containing tellurium, as the ethereal bromine mixture has a solvent action on tellurium, as well as on tellurous acid and tellurium gold; stannous chloride produces a black precipitate of tellurium in gold solutions which contain tellurium, which may completely conceal the purple coloration produced by the gold.

By means of the Döring method, it is possible to detect the gold in ores containing 0.5 g. per ton (about 8 grains per ton).

**Gold in Electro-plating Baths.**—In gold baths, which contain a large quantity of potassium cyanide besides gold potassium cyanide, the gold is estimated as follows:—Fifty cubic centimetres are treated in a 500 c.c. porcelain dish, in a draught chamber, with 30 c.c. of 25 per cent. hydrochloric acid. The dish, covered at first with a clock-glass, is warmed on a water-bath, at the end of ten minutes the cover-glass removed, the solution evaporated down to about 20 c.c., a hydrochloric acid solution containing 5 g. of stannous chloride added, and the heating continued for a further quarter of an hour; 100 c.c. of water are then added, the whole filtered through a strong (or double) filter paper, the residue washed on the filter paper with boiling water, and any residue adhering to the dish removed with a piece of moistened filter paper and added to the rest. The filter is dried, burnt in a porcelain crucible, and the residue melted into 5 g. of granulated assay lead, the button thus obtained being cupelled. If the gold button be not a full yellow, and therefore contains silver, it is parted according to the directions given on p. 129.

Instead of taking up the "purple of Cassius" precipitate with lead, it may be strongly heated by itself in a porcelain crucible, and then warmed on a water-bath with 5 c.c. of hydrochloric acid and 0.5 c.c. of nitric acid, the crucible being at first covered with a watch-glass. The solution obtained is evaporated, taken up with water containing a little hydrochloric acid, filtered, and the gold precipitated with ferrous sulphate, instead of with oxalic acid, on account of the copper usually present. The precipitate is filtered through a double ash-free paper, washed, dried, burnt in a porcelain crucible, and the pure gold weighed.

The potassium cyanide content of baths is either estimated volumetrically, according to the method described in Vol. I., p. 550, or 1 c.c. of the solution is diluted with 20 c.c. of water, silver nitrate added in excess (equivalent to 0.1 or 0.2 g. silver), the solution stirred, 5 c.c. of nitric acid (sp. gr. 1.2) added, and the whole allowed to stand

for several hours. The precipitate is then filtered, washed, and dried, the filter and its contents heated in a porcelain crucible and the carbonaceous matter burnt off; after a final strong heating, the auriferous silver is weighed. The gold contained in 1 c.c. of bath solution is deducted.  $\text{KCN} = \text{Ag} \times 0.6035$ .

Gold baths usually contain from 1 to 3 g. gold, and from 5 to 20 g. potassium cyanide per litre. When gold chloride is used for the preparation of the bath, instead of the double cyanide, this potassium cyanide determination comes out somewhat too high, on account of the silver cyanide precipitate containing silver chloride.

According to Silva,<sup>1</sup> gold and platinum can be precipitated in the metallic state, and pure, from solutions, which contain also chlorides of tin, antimony, and arsenic, by addition of an excess of sodium hydroxide solution, followed by chloral hydrate, and then warming.

## II.—THE ASSAY OF GOLD ALLOYS

The materials for assay are chiefly rich gold bullion, which contains but little silver, copper, and platinum metals, alloys of gold with copper (coinage alloys), gold with silver, gold with silver and copper, and in addition, industrial alloys of low standard containing up to 10 per cent. of zinc, amalgams, auriferous platinum, and gold-platinum alloys (*cf.* Platinum, p. 148), auriferous lead, bismuth, antimony, and alloys of more or less indefinite composition resulting from the treatment of scrap, lemel, sweep, etc.

**Parting with Nitric Acid. Inquartation with Silver.**—The parting of beads obtained in ore assays is described on p. 129. Alloys of gold with silver and copper are also usually parted with nitric acid.

If the gold is alloyed with an excess of silver, or if the alloys contain much copper or other base metals, the gold remains behind in powder form after treatment of the alloy with hot nitric acid.

The approximate gold content of rich alloys is ascertained by a preliminary assay, and then a gold-silver alloy is made, in which the relation of gold to silver is 1 to 2.5 or 1 to 3 (hence the term "inquartation"). A strip is then rolled out and made into the form of a loose spiral, which is boiled in a parting-flask with pure nitric acid, until the silver is completely dissolved out; the porous gold is washed with hot distilled water, then transferred to a small unglazed annealing cup, dried and ignited, and the pure gold weighed.

When the gold content in the alloy is known, and only requires to be checked, as is the case with gold-copper coinage, the silver-gold alloy is obtained on a cupel in the muffle by direct cupellation with the calculated amount of silver for inquartation and the necessary quantity of lead.

<sup>1</sup> *Z. anal. Chem.*, 1889, 28, 701.

## A. PRELIMINARY ASSAY

## 1. Alloys which do not contain Copper.

**Touchstone Assay.**—The streak produced on a touchstone is compared with those of “needles” of known fineness.

Concentrated nitric acid should not completely dissolve the streak, and the gold should remain undissolved; this forms a method of distinction from imitation gold alloys.

Or, the bead obtained by cupellation of the original gold-silver-copper alloy with assay lead (*cf.* 2, Cupreous Alloys) is compared with those obtained from standard alloys containing 600, 700, 800, 900 thousandths of gold, and with a bead from pure gold, all fixed on a white card and surrounded with a black edging.

For such comparative purposes, tiny plates of gold-silver alloys, a considerable number of which, with gradually increasing gold content, are attached to a porcelain plate, can also be used.<sup>1</sup>

When the percentage of silver reaches 56, the gold content cannot be judged from the colour; such alloys are white; 2 per cent of silver will change a gold-coloured alloy to a brass colour.

Full yellow alloys require two and a half to three times their own weight of silver, light yellow alloys twice their weight, and white alloys their own weight. As an example, suppose that by comparison with standard beads, the gold content of the alloys is estimated at between 700 and 800 thousandths, the amount of silver required for the usual assay weight of 500 mg. is calculated as follows:—Anything between 700 and 800 is taken as 700; consequently, in 500 mg. of the alloy, there are  $0.7 \times 500 = 350$  mg. of gold and 150 mg. of silver. Now 350 mg. of gold require  $3 \times 350 = 1050$  mg. of silver; 150 mg. of silver are already present in the alloy, so that 900 mg. of assay silver must be weighed out and cupelled with the alloy. Should the original estimate have been too low, and the gold be exactly 800 per 1000, the amount of silver taken, 900, would still be ample for parting, since the relation of gold to silver would be 400 to  $(900 + 100)$  or 1 to 2.5. Usually the inquartation silver used is two and a half times the weight of the gold.

In the case of white alloys, the gold content of which cannot be approximately gauged in the manner described, and which are alloyed with an equal weight of silver, coherent gold is only obtained on parting if the gold content of the original alloy is not much under 500 per 1000. Otherwise the gold remains as a powder and requires more care in decantation and collecting.

<sup>1</sup> Goldschmidt, *Z. anal. Chem.*, 1878, 17, 142; *Berg. u. Hütten. Zeit.*, 1878, 37, 208.



## 2. Alloys which contain Copper.

For alloys that contain no silver, the touchstone assay is applicable, needles consisting of gold-copper alloys of known composition being employed. Even small quantities of silver, zinc, etc., in the gold-copper alloy have, however, quite an appreciable effect on the colour of the alloy.

The usual preliminary assay consists in cupelling from 250 to 500 mg. of the alloy with eight to twenty-five times its weight of assay lead, according to the amount of copper present, just as in the case of the silver assay (p. 111), except that a somewhat higher temperature must be employed, because copper is more difficult to oxidise completely in presence of gold. The loss in weight gives the amount of copper and other base metals, and, by comparison of the bead with standard beads, the quantity of inquartation silver required for the assay proper is ascertained.

### B. THE ASSAY PROPER

**Cornet Assay.**<sup>1</sup>—The method presupposes an approximate estimation of the gold, silver, and copper by a preliminary assay, and varies in minor details in nearly every laboratory.<sup>2</sup>

Two portions of exactly 500 mg. each, consisting of flattened pieces or drillings (from the upper and lower parts, in the case of ingots), are weighed out on a sensitive balance, and the requisite quantity of silver for inquartation added;<sup>3</sup> the mixtures are wrapped in pure lead foil, and are put, with the necessary number of units of assay lead, on to a small tray and taken to the muffle furnace, containing a number of ready heated cupels. The lead is put into two cupels in the centre of the muffle and allowed to melt and “uncover” in the closed muffle; the small packets of sample and silver are then introduced, the muffle closed until cupellation begins, when it is again opened and the operation carried out, as in the case of a silver assay. Litharge crystals should not appear. A higher temperature must be employed than in the case of the silver assay, owing to the higher melting point of gold. The maintenance of the proper temperature during cupellation has a considerable influence on the results.

J. Prinsep, as long ago as 1828, made use of silver-gold and gold-platinum alloys for controlling the furnace temperature. Since the introduction of the Le Chatelier thermo-electrical pyrometer (see Vol. I., pp. 180 *et seq.*), it has been possible to fix the proper temperature for the assay of gold alloys by accurate experiments. T. Kirke Rose

<sup>1</sup> Cf. Kerl, *Metallurgische Probierkunst*, 2nd edition, pp. 367 *et seq.*

<sup>2</sup> Cf. Claudet, *Trans. Inst. Min. and Met.*, 1906-7, 16, 136.

<sup>3</sup> Cf. E. A. Smith, *J. Inst. of Metals*, 1910, 3, 105.



has published a complete series of experiments in this connection.<sup>1</sup> He concludes that the mean temperature of the muffle during cupellation should be  $1060^{\circ}$  to  $1065^{\circ}$ ; each  $5^{\circ}$  above this means a loss of gold to the extent of 0.01 per 1000.

W. Witter<sup>2</sup> has investigated the influence of temperature on the accuracy of gold assays, and concludes that the best temperature for the cupellation of coinage gold (900 gold to 100 copper) is  $930^{\circ}$  of pure gold  $950^{\circ}$  to  $960^{\circ}$ , and of gold containing a little platinum  $1000^{\circ}$  to  $1010^{\circ}$ .

The assays, after they have "brightened," are drawn forward in the muffle, and after setting, whereby a slight sinking of the surface takes place, they are removed altogether. The beads are detached by fine-nosed pliers, brushed on the under side, well squeezed with the pliers, and brushed again until the under surface is clean. The beads are then flattened on an anvil with a polished steel hammer, and the flattened bead heated to redness in the muffle on a piece of porcelain, and rolled out. No cracks should show at the edges on rolling. The rolled pieces are annealed, numbered by stamping, rolled on to a thick glass rod, and the cornets then slacked out.

In the Berlin Mint, where 250 mg. of bar-gold, 562.5 mg. of silver, and 4 g. of lead are taken, the beads, rolled to a thickness of 0.5 mm. and a width of 12 mm., have a length of about 25 mm.

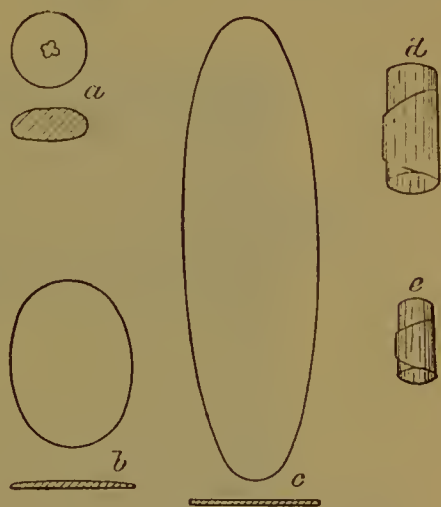


FIG. 49.

The accompanying illustrations<sup>3</sup> (Fig. 49) show the bead, *a*; flattened bead, *b*; rolled strip, *c*; cornet, *d*; and annealed cornet, after parting, *e*, all in natural size, as obtained at the London Mint from 500 mg. gold, etc.

The cornets are now boiled in a parting-flask with nitric acid. The parting-flasks are long-necked flasks of well-annealed potash-glass (or Jena glass), about 200 mm. in length, 50 mm. wide in the body, and 20 mm. wide at the end of the neck. Into these are introduced 20 c.c. of pure nitric acid of sp. gr. 1.2, free from chlorine, nitrous acid, and selenic acid. Each is placed on a stand (Fig. 50) over a rose-burner, and the acid is heated nearly to boiling; the cornets are introduced, and boiling is continued for ten minutes after nitrous fumes have disappeared.

<sup>1</sup> *J. Chem. Soc.*, 1893, 63, 707. Cf. also, *The Metallurgy of Gold*, T. K. Rose, 5th edition, 1906, pp. 470 *et seq.*, and *J. Soc. Chem. Ind.*, 1893, 12, 359.

<sup>2</sup> *Chem Zeit.*, 1889, 23, 522.

<sup>3</sup> From Rose's *Metallurgy of Gold*, 5th edition, p. 479.

The flasks are removed from the stand with a cork-lined spring clamp, the acid carefully poured off into a porcelain vessel, and the cornets washed with hot distilled water, by decantation; about 20 c.c. of hot pure nitric acid, of sp. gr. 1.3, are now added, and the boiling continued for from fifteen to twenty minutes, to complete, as far as possible, the solution of the traces of silver still remaining in the gold; this can be effected so as to leave a residue of from 0.1 to 0.14 per cent. To prevent bumping of the concentrated acid during the second boiling, a piece of wood-charcoal is introduced, or a charred pea or charred peppercorn.

After the second boiling, the acid is again poured off and the cornet washed twice with hot distilled water, the flask being filled

completely from a glass vessel each time, whilst held in a slanting position.

After the washing is completed, the flask is once more filled with water and carefully inverted in a small unglazed annealing cup. The brittle dark brown gold cornet falls into the cup; the water is allowed to escape gradually from the flask by allowing it to overflow from the cup into a beaker. The water in the cup is then poured off as completely as possible, the slight remainder being absorbed by means of a strip of filter paper, care being

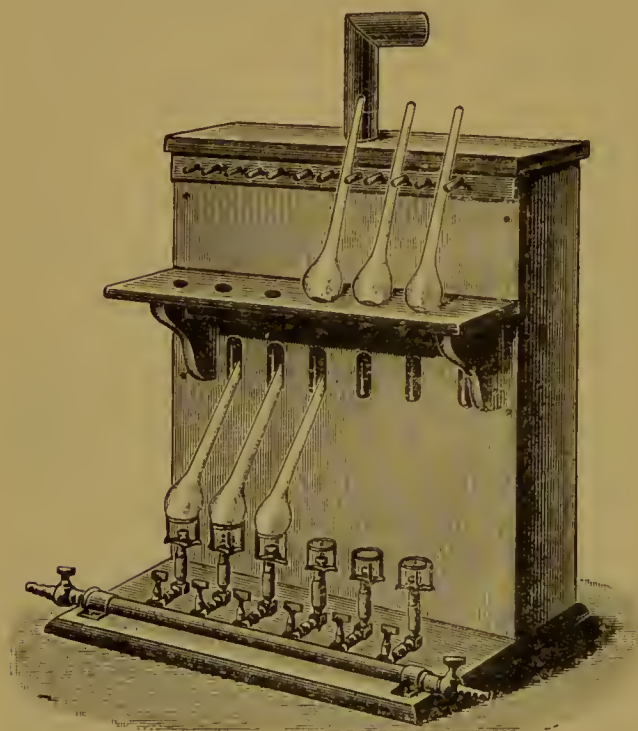


FIG. 50.

taken that no gold is removed; the cup is dried for five minutes in front of the muffle, and then heated for a minute or two in the muffle to a bright red heat. The gold shrinks to about one-third of its former size, and becomes golden yellow in colour, lustrous, and coherent. The stamped number is distinctly visible. The cornet is then transferred to the pan of an assay balance and weighed to within 0.1 to 0.05 mg. The mean of the assays of "upper" and "lower" samples is taken as the true assay of the bar.

For simultaneously boiling a large number of samples, up to, say, 100, a very convenient form of platinum apparatus made by Johnson, Matthey & Co., is employed in the mints in London,

Berlin, and other places.<sup>1</sup> Parting cruets made of silica are also obtainable.

The results of assays of gold alloys are reported either decimally or by the "carat" system.<sup>2</sup> The decimal system is now being more generally adopted, but the older "carat" system is still largely used in England, as the workers and dealers in gold and silver alloys prefer this method of valuation. In these reports the alloys are referred to standard gold, 22 carat (916.6 per 1000), pure gold being 24 carat. The gold carat contains 4 grains, and the grain is subdivided into eight parts. In reporting how much gold in carats, grains, and eighths is present in an alloy above or below the legal "standard," the conventional terms "betterness" or "worseness" are used, the metal being reported as B<sup>r</sup> when above standard and W<sup>o</sup> when below; for example, a sample of 18-carat gold would be reported as 4 carats worse, the report reading:—

<i>Gold Report.</i>		Carats.	Grains.
W <sup>o</sup>	. . . . .	4	...
Standard, 22 carats.			

In the reports of "parting" assays, in which both the gold and silver are returned in ounces of fine gold and silver in one pound troy, the abbreviations F.G. (fine gold) and F.S. (fine silver) are very frequently employed.

With regard to the accuracy of the cornet assay, Rose states that, with careful working, the error does not exceed  $\pm 0.02$  per 1000; this is confirmed by the very careful experiments of W. Witter.<sup>3</sup> The unavoidable loss of gold by absorption in the cupel and by volatilisation is almost exactly counterbalanced by the 1.2 to 1.4 parts per 1000 of silver remaining in the cornet.

In order to have a check on more material losses of gold, caused by an excessive temperature during cupellation, solution of gold, etc., check assays are frequently made, using pure gold, pure copper, and the same amount of silver and assay lead as are used in the assay itself, such check assays being cupelled alongside the assays proper. These checks generally show a surcharge of 0.1 to 0.4 per 1000, which has to be deducted from the assay values found.

Pure gold (assay gold) for this purpose was prepared by Roberts-Austen, at the London Mint, as follows:<sup>4</sup>—Cornets obtained from gold of a high degree of fineness were dissolved in aqua regia, excess of

<sup>1</sup> Kerl, *Metallurgische Probierkunst*, 2nd ed., p. 374; for particulars of construction, see Jarman, *Trans. Inst. Min. and Met.*, 1905-6, 15, 625.

<sup>2</sup> Cf. E. A. Smith, *J. Inst. Metals*, 1910, 3, 122.

<sup>3</sup> *Chem. Zeit.*, 1899, 23, 522; *J. Soc. Chem. Ind.*, 1899, 18, 768.

<sup>4</sup> *Fourth Annual Report of the London Mint*, 1873, p. 46.



acid removed by evaporation, and platinum precipitated by addition of potassium chloride and alcohol to the concentrated solution. The filtered gold solution, after diluting considerably with distilled water so that the strength was about 15 g. gold to 4.5 litres, was allowed to stand for about three weeks, to ensure precipitation of silver chloride; the clear liquid was then syphoned off, and the gold from 4.5 litres of solution precipitated in spongy condition, in the course of four days, by the frequent addition of small quantities of pure oxalic acid, the solution being gently warmed during the precipitation. This was then repeatedly digested with hydrochloric acid, distilled water, and ammonia, and finally washed with distilled water, dried, and melted in a clay crucible, with acid potassium sulphate and borax. The purified gold was cast in a marble mould.

C. Whitehead<sup>1</sup> evaporates the gold chloride solution to dryness, dissolves the residue in water with the addition of a few cubic centimetres of hydrobromic acid, and dilutes the solution from 10 g. gold to 1.5 litre. The gold is precipitated from the absolutely clear syphoned solution by means of sulphur dioxide, again dissolved, and the above treatment repeated, the gold being finally washed, dried, and melted with borax and nitre.

The following modification of the ordinary assay is due to Bock.<sup>2</sup> Cupellation, with its attendant loss of gold, is avoided by alloying the rich bullion with the requisite amount of silver in a small graphite crucible, flattening out the button, re-melting, and then making the cornet, and boiling in the usual way twice with nitric acid; the minute remainder of silver is then removed electrolytically, by subjecting the cornet for ten minutes, in a platinum crucible, to a current not exceeding 1 ampère per square metre of cathode surface, the electrolyte consisting of very weak nitric acid (one volume nitric acid of sp. gr. 1.2 to five volumes of water).

An examination of this method by Witter and Bock, in the Staatshütten laboratory at Hamburg, showed the results to be excellent. It is unfortunately unsuitable for brittle gold, which, even when alloyed with silver, cannot be either beaten out or rolled, but it is well suited for malleable gold and malleable gold-silver-copper alloys.

**Influence of Platinum Metals on the Mint Assay.**—Platinum and platinum metals are frequently contained in gold bullion, and their presence is undesirable; gold, containing much of these metals, is not bought by the mints.

*Platinum.* The presence of small quantities of platinum in gold is indicated by the rough, crystalline appearance of the surface of the bead, obtained by cupelling without addition of silver; larger quantities are

<sup>1</sup> *Eng. and Mining J.*, 1899, 68, 785; *J. Soc. Chem. Ind.*, 19, 1900, 148.

<sup>2</sup> *Chem. Zeit.*, 1897, 21, 973; 1898, 22, 358; 1899, 23, 49; *J. Soc. Chem. Ind.*, 1898, 17, 695.



indicated by the grey colour of the bead. Platinum is separated from gold by cupelling the cornet obtained in the assay with eight times its weight of silver and lead, boiling with nitric acid, weighing the gold powder produced, repetition of the alloying with silver, boiling, and so on, until the gold obtained is of constant weight.<sup>1</sup>

Priwoznik<sup>2</sup> states that platinum, to the extent of 2 per cent. of the weight of the gold, goes into solution in nitric acid along with the silver, the solution being colourless; traces of palladium, however, produce a pale yellow, and more palladium a brownish to reddish brown colour.

J. Spiller<sup>3</sup> states that the best solvent for platinum-silver is hot nitric acid of sp. gr. 1.42, which dissolves 0.75 to 1.25 per cent. of platinum along with the silver. Weak acid of sp. gr. 1.2 dissolves only 0.25 per cent. of platinum; the strongest acid is unsuitable, and brings about a separation of platinum black.

H. Carmichael<sup>4</sup> has shown that the solution of platinum is influenced by the proportion of platinum to gold, as well as by that of platinum to silver. For example, an alloy consisting of platinum 5 to 7 mg., gold 100 mg., silver 400 mg., on being boiled first in nitric acid of sp. gr. 1.171, followed by a second acid of sp. gr. 1.285, parted completely, all the platinum going into solution. Mass action seems to play a part in this process, for whereas the above alloy parted completely, an alloy consisting of platinum 14 mg., gold 200 mg., silver 800 mg., did not part, although an alloy of platinum 14 mg., gold 300 mg., silver 900 mg., parted completely.

From these results it will be seen that there should be about twenty times as much gold as platinum, and about three times as much silver as gold present, in order to part the gold completely from platinum and silver by means of nitric acid.

*Palladium.* According to Priwoznik, palladium cannot produce any considerable error in gold assays, as an alloy of 102 parts of palladium and 1250 parts of silver dissolves completely in strong nitric acid, forming a reddish brown solution.

*Iridium* in gold produces, on cupellation with silver and lead, rough, dark-spotted beads, from which rough, blistered, dark-grey to black-spotted cornets are obtained, in which iridium can be detected in the blisters.

In assay laboratories, *Iridium* and *Osmiridium* are usually separated

<sup>1</sup> Cf. C. Winkler, "Solubility of Platinum Silver in Nitric Acid," *Z. anal. Chem.*, 1874, **13**, 369; *J. Chem. Soc.*, 1875, **28**, 428; see also, Oehmschen, *Berg. u. Hütten. Zeit.*, 1901, **60**, 137; *J. Soc. Chem. Ind.*, 1901, **20**, 507.

<sup>2</sup> *Berg. u. Hütten. Zeit.*, 1895, **44**, 325; cf. also, *Oesterr. Zeitschrift f. Berg. u. Hütten.*, **47**, 356; *J. Chem. Soc. Abstr.*, 1900, **78**, 111.

<sup>3</sup> *Proc. Chem. Soc.*, 1897, **18**, 118; *Chem. Zeit.*, 1897, **21**, 477; *J. Soc. Chem. Ind.*, 1897, **16**, 539.

<sup>4</sup> *J. Soc. Chem. Ind.*, 1903, **22**, 1324.

from the gold, alloyed with two or three times its weight of silver, before treatment with sulphuric acid, by allowing the alloy to stand in the crucible for half to three-quarters of an hour, after stirring. The iridium and osmiridium sink to the bottom.

The presence of *Rhodium* causes high results to be obtained in the gold assay. Iridium and rhodium remain almost entirely undissolved when the cornet is treated with aqua regia.

*Ruthenium* produces considerable liability to spitting of the cupelled bead. On cooling, such beads appear greyish black with a blue and green sheen in spots where spitting has not taken place.

*Osmium* volatilises during cupellation, in the form of perosmic acid.

**Determination of Gold in Gold-Silver-Copper Alloys and in Auriferous Silver.**—Two lots of 0.5 g. of the alloy are cupelled with sixteen times to thirty-two times the weight of assay lead, the percentage of base metal ascertained by loss, the bead alloyed, if necessary, with silver, and parted by boiling with nitric acid, etc.

In American mints and in the more important commercial laboratories in New York, according to C. Whitehead and T. Ulke,<sup>1</sup> the noble metals in gold-silver alloys, rich in copper, are estimated as follows:—Ten grams of the sample are attacked by boiling with 100 c.c. of nitric acid (sp. gr. 1.2), the solution diluted to 300 c.c., and the gold collected on a filter; this is then dried, 2.5 g. of granulated lead added on the filter, which is then folded up and dipped into 5 g. of lead already melted on a scorifier; after limited scorification, the melt is poured and the button freed from slag and cupelled.

The hot filtrate from the gold is treated with a sufficiency of common salt and well agitated by means of compressed air. If over 0.06 per cent. of silver be present in the alloy, the silver chloride settles in the course of half an hour. On account of the presence of traces of gold, filtration is effected through a double filter, and 2.5 g. of granulated lead are added on the filter. The whole is dried on a scorifier over the muffle, the paper then burnt by placing it in the muffle, 15 g. of lead and 0.5 of borax added, and the whole scorified. The button, which should weigh about 4 g., is cupelled, and the weighed bead parted.

R. van Liew<sup>2</sup> reduces the gold loss experienced on dissolving copper containing noble metals in nitric acid, by lowering the working temperature. An assay ton of drillings is treated at ordinary temperature with 350 c.c. of water and 100 c.c. of nitric acid (sp. gr. 1.42); the solution occupies twenty-four hours. Air is then blown through the solution, 2 to 4 c.c. of normal salt solution added, and after standing for twelve hours, the precipitate is collected on a filter and

<sup>1</sup> *Eng. and Min. J.*, 1898, 65 [7], 189; *J. Soc. Chem. Ind.*, 1898, 17, 379; *Chem. Zeit. Rep.*, 1898, 22, 69.

<sup>2</sup> *Eng. and Min. J.*, 1900, 69, 469, 498; *Chem. Zeit. Rep.*, 1900, 24, 147.

washed. From 4 to 6 g. of assay lead are then added on the dried filter, the filter incinerated on a scorifier outside the muffle, and the scorification carried out with the addition of 3 or 4 g. of litharge and 3 or 4 g. of fused borax. This is followed by cupellation and parting.

Lindemann<sup>1</sup> dissolves 10 g. of crude silver in a long-necked flask in 80 to 100 c.c. of nitric acid (sp. gr. 1.2) decants the silver solution into a litre flask, and then boils the residual gold again with nitric acid; the solution is again decanted, the residue washed repeatedly with hot distilled water, all the wash water united in the litre flask, and the gold collected in a tiny crucible, dried, ignited, and weighed.

The silver solution is cooled to the ordinary temperature, and diluted to exactly 1 litre; 100 c.c. (corresponding to 1 g. of the sample) are then titrated with ammonium thiocyanate (*cf.* Vol. I., p. 123, and Silver, p. 116).

Oehmischen<sup>2</sup> treats gold alloys, containing tin and zinc, by scorification with twenty times their weight of assay lead and a quarter their weight of borax, then cupels the lead button, and so on.

**Inquartation with Cadmium.**—This method, due to Balling,<sup>3</sup> is carried out without cupellation in a muffle, and allows, furthermore, of an accurate determination of silver in one and the same sample.

According to Kraus,<sup>4</sup> satisfactory results are obtained by the following modification:—About 3 g. of potassium cyanide are melted in a small porcelain crucible, over a gas flame or a spirit lamp, 250 mg. of the alloy (gold bullion) added, and then two and a half times its weight of cadmium; after melting down, the whole is shaken round, whereupon a silver-white mobile alloy is produced. After cooling, the potassium cyanide is removed by water, the button (or, if two samples are treated, both buttons) transferred to a parting flask and treated with nitric acid (sp. gr. 1.2), a charred pea being introduced, and the whole heated for some time; in the case of fine gold, the boiling occupies one hour. The solution is decanted, and the residue washed once with hot water, after which it is boiled for ten minutes with nitric acid of sp. gr. 1.3, the solution poured off, the residue washed with hot water, and boiled for five minutes with water, which is then poured off; the flask is then filled with water, the gold transferred to a small porcelain crucible, dried, and ignited, and the beads weighed, either separately or together.

If the decanted acid and washings are collected, the silver can be determined as silver chloride, after evaporation, or it can be estimated volumetrically by the Volhard method (p. 116).

<sup>1</sup> *Z. anal. Chem.*, 1877, 16, 361.

<sup>2</sup> *Z. angew. Chem.*, 1895, 8, 133; *J. Chem. Soc. Abstr.*, 1895, 68, 295.

<sup>3</sup> *Oesterr. Zeitschrift*, 1879, p. 597; 1881, No. 3.

<sup>4</sup> *Dingl. polyt. J.*, 1880, 236, 323; *Berg. u. Hütten. Zeit.*, 1880, 39, 219; *J. Chem. Soc. Abstr.*, 1880, 38, 679.



The cadmium alloy is brittle and cannot be flattened; consequently, long-continued boiling of the bead with nitric acid is necessary; the final boiling with water must also be very thorough, in order to remove the last traces of cadmium nitrate.

**Estimation of Gold in various Alloys.**—Alloys rich in copper may be assayed by scorification and cupellation, or by the combined wet and dry method (*cf.* p. 109). If the copper be small in amount, the alloy may be cupelled, according to Kerl, with addition of silver; the silver must be about three times the reputed gold content, otherwise the gold bead will contain copper.

Kerl states that with *gold amalgam* the mercury must be distilled off in a hard-glass retort, and the residue of spongy gold scorified with eight times its weight of assay lead, the temperature being gradually raised.

*Lead* and *Bismuth-gold alloys* are cupelled direct, but poor alloys should be first concentrated.

*Auriferous antimony* may be assayed as follows:<sup>1</sup>—Thirty grams of powdered antimony are mixed with 60 g. of litharge, 12 g. of nitre, and 12 g. of sodium carbonate, and melted in a crucible for a quarter of an hour at a low red heat in a wind-furnace; the melt is poured into a mould, and the button cupelled. The slag from the melt is run down with 30 g. of litharge and 1.2 g. of charcoal; the button from this is also cupelled.

For the assay of alloys of gold with platinum and the platinum metals, *cf.* Platinum, p. 148.

**Electrolytic Estimations of Gold.**—Gold is seldom estimated electrolytically.<sup>2</sup>

**Imitation Gold Alloys.**—According to Weber, these alloys show a black coloration on the surface when treated with one drop of a concentrated solution of cupric chloride; the surface should be first cleaned with alcohol and ether. Gold alloys, and even thinly-plated goods, do not react thus. Solutions of silver nitrate and gold chloride exert a similar action. The streak produced on the touchstone by imitation alloys disappears on treatment with strong nitric acid.

Very thin plating is detectable, according to R. Finkener, by taking a piece of material weighing 0.1 to 1.5 g., washing with alcohol and ether, and then treating it in a beaker with 0.5 to 10 c.c. of pure nitric acid (sp. gr. 1.3). Tiny gold leaflets are soon observable on the bottom of the beaker and also floating on the surface of the liquid.

If wash-gilded material is similarly treated, the more coherent gold particles appear rough on the under side and are somewhat darker in colour.

<sup>1</sup> E. A. Smith, *J. Soc. Chem. Ind.*, 1893, 12, 316; *Chem. News*, 1893, 67, 195.

<sup>2</sup> *Cf. Quantitative Chemical Analysis by Electrolysis*, A. Classen, translated by B. Boltwood, 1903.



## PLATINUM

Platinum ores, the metal itself, and the platinum metals and their alloys, are seldom assayed in commercial laboratories. Their content and value are almost exclusively determined in the laboratories of the dealers in St Petersburg, London, Hanau, Frankfort-on-Main, Paris, and New York, whither also worn-out sulphuric acid pans and old platinum laboratory utensils are sent to be re-worked.

The quantitative separation of the individual platinum metals is a matter of considerable difficulty.

The raw materials for the manufacture of platinum and the platinum metals are :—

*Native Platinum*, obtained by washing alluvial deposits, and usually accompanied by gold, osmiridium, and many specifically heavy minerals, such as chrome iron ore, titanite iron ore, magnetite, zircon, spinelle, etc.

*Sperrylite*,  $\text{PtAs}_2$ , containing a little rhodium and antimony, found only in Canada, accompanying nickel ores.

The *Platinum Metals*, obtained in the parting of gold-silver alloys and in the electrolytic separation of gold.

*Russian 3, 6, and 12 rouble pieces*, struck in the thirtieth and fiftieth years of the nineteenth century, and kept in circulation for a short time.

Native platinum (washed platinum) contains, on the average, according to Kerl,<sup>1</sup> from 80 to 86 per cent. of platinum, 1 to 8 per cent. of iridium, 1 to 8 per cent. of osmiridium, 0.25 to 2 per cent. of palladium, 0.4 to 3 per cent. of rhodium and ruthenium, 5 to 13 per cent. of iron and copper, and 1 to 4 per cent. of sand. In the ore from the Urals, the content of iridium, rhodium, and palladium together is usually 4 to 5 per cent., and the residue, insoluble in aqua regia and consisting chiefly of osmiridium, is about 8 per cent.

Good ores, as a rule, have a specific gravity of 16 to 17 ; large pieces containing veins of chrome iron ore, etc., are appreciably lighter. Pufahl found the specific gravity of such a piece from Nischne-Tagilsk to be 12.304.

ASSAY METHODS FOR ORES<sup>2</sup>

Originally the ores were assayed and worked in the wet way ; a combination of wet and dry processes is now employed.

Deville and Debray's Dry Method for Platinum Sand.<sup>3</sup>

1. *Gangue* (Quartz, Chromite, Titanite Iron Ore, etc.). Several samples, of 2 g. each, are fused with 7 to 10 g. of fine silver, under a

<sup>1</sup> *Muspratt-Stohmann's Handbuch der technischen Chemie*, 4th edition, vol. vii. (1898), p. 260.

<sup>2</sup> Cf. *ibid.*

<sup>3</sup> *Ann. Chim. Phys.*, 1859 (iii.), 56, 385 ; *Berg. u. Hütten. Zeit.*, 1860, 19, 256.

layer of 10 g. of borax, in small, glazed, clay crucibles. The temperature must be considerably above the melting point of silver. The borax is well stirred with the stem of a clay pipe and the whole is allowed to cool, when the borax and other material are separated from the metallic button, warming with dilute sulphuric acid and hydrofluoric acid being resorted to, if necessary. The difference in weight of the button and that of the ore plus silver gives the weight of gangue.

2. *Gold.* An average sample, weighing 10 g., is boiled continuously for several hours with mercury, frequent small additions of mercury being made from time to time. The whole of the mercury is run through a pierced filter, the mercury distilled off in a small glass retort, and the residue of spongy gold strongly heated and weighed. The results are tolerably accurate, but, as a rule, too low to a negligible extent.

Instead of boiling with mercury, the ore may be made into a thick pulp with water, and then ground with mercury for some hours in an iron mortar. The residue is then washed from the mercury and the latter treated as above (Bannister).

According to W. Duprè,<sup>1</sup> gold, precipitated electrolytically in a platinum dish, dissolves easily in a solution of common salt saturated with chromic acid, without the platinum being attacked; Classen confirms this. This solvent for gold might, therefore, be made use of in the estimation of gold in platinum ores.

3. *Platinum.* Fifty grams of ore are fused with 75 g. of assay lead and 50 g. of pure galena, in a fire-clay crucible, under a layer of 15 g. of borax, the mixing being effected with the stem of a clay pipe, until all the beads are dissolved; the temperature is gradually raised to the melting point of silver, then 50 g. of litharge are added, and the temperature still further raised for a short time. The platinum metals (except osmiridium) alloy with the lead, and osmiridium collects at the bottom. The sulphides of copper and iron, produced through the agency of the galena, are oxidised by the litharge, and the oxide is slagged. When evolution of sulphur dioxide has ceased, the crucible is allowed to cool, and the button, which weighs about 200 g., cleaned; the lower portion is then sawn off, to the extent of about one-tenth of the bead, and weighed. The main portion of the hard alloy, together with the grains from the sawing, is weighed and powdered, and one-ninth of it is cupelled.

A considerable amount of lead, at least 6 or 7 per cent., remains with the platinum; according to Deville and Debray's process, it is removed by an oxidising fusion in a small lime furnace, using an oxyhydrogen flame with excess of oxygen.

To avoid this treatment, the lead-platinum alloy can be cupelled, at a high temperature, with five to six times its weight of silver

<sup>1</sup> Cf. Classen, *Quantitative Chemical Analysis by Electrolysis*, translated by Boltwood.

(accurately weighed), and, in addition, assay lead. The increase in weight of the silver gives the platinum content of one-ninth of the total, so that nine times this value gives the amount in the whole upper portion of the lead-platinum alloy.

The silver-platinum alloy, after being rolled out quite thin, can be parted by continued boiling with concentrated sulphuric acid.

The lower tenth of the large lead-platinum button, which was sawn off, is broken down and warmed for some time with ten times its weight of nitric acid (sp. gr. 1.2) and an equal quantity of water, in order to dissolve out the lead; the residue, consisting of osmiridium prills and leaflets and platinum black, is thoroughly washed by decantation, first with hot water containing nitric acid, and finally with hot water, then dried and weighed. The platinum is then dissolved out with hot aqua regia and the unchanged osmiridium washed, dried, and weighed.

The percentage of platinum with platinum metals, and also that of osmiridium, is thus ascertained.

The pure platinum contained in the ore is from 4 to 5 per cent. less than the amount found, since the platinum in Russian ore is alloyed, fairly evenly, with 4 to 5 per cent. of the other platinum metals; the percentage of osmiridium, however, varies considerably.

The following is a very suitable method for the examination of platinum-bearing sands, etc. The crushed material is fluxed in a pot with red lead, etc., in order to obtain a lead button, as described under the assay of silver and gold ores. The lead button is cupelled, and the resulting bead rolled out and boiled in dilute sulphuric acid, the acid being gradually allowed to get stronger. The residue is washed, boiled in nitric acid, and again washed. The two resulting solutions contain the silver. The residue is then dissolved in aqua regia. Osmiridium remains, together with a trace of silver chloride and lead sulphate; the silver chloride may be dissolved in ammonia, and the lead sulphate in ammonium acetate solution. The osmiridium is then washed, weighed, and further examined, if necessary. The aqua regia solution contains platinum and gold; platinum may be precipitated by ammonium chloride, and gold by ferrous sulphate (Bannister).

### Wet Assay for Ores.

In the St Petersburg Mint 5 to 10 g. of gold-free ore are repeatedly digested for eight or ten hours in a porcelain dish with aqua regia (one volume nitric acid of sp. gr. 1.34 to three volumes hydrochloric acid), until a yellow solution is no longer obtainable. A concentrated solution of ammonium chloride is added to the solution, which contains platinum, iridium, palladium, rhodium, etc., and the precipitate, coloured red by iridium, is transferred to a filter, washed with alcohol, dried, and gently ignited. On prolonged digestion of this residue with consider-



ably diluted aqua regia (1:4 or 1:5) at 40°, only platinum goes into solution. From the difference between the weight of the platinum black containing iridium and that of the iridium obtained, the amount of pure platinum is ascertained.

The following method, due to Hess,<sup>1</sup> can be recommended. The ore is fused with four times its weight of zinc, and the finely powdered alloy treated first with weak, then with strong sulphuric acid, whereby the zinc is dissolved; the copper and lead are then dissolved out with nitric acid, and the washed residue treated with aqua regia. The separation of platinum, etc., is effected as above.

Miller<sup>2</sup> scorifies platinum ores with assay lead, then dissolves out the lead by warming the button with dilute nitric acid of sp. gr. 1.05, oxidises the residue by roasting, and boils again for ten minutes with nitric acid. The washed and dried residue is weighed as crude platinum. Should it contain gold, it is treated with weak aqua regia (1:5), the filtered platinum-gold solution evaporated to dryness, very weak hydrochloric acid added, and the gold precipitated with oxalic acid, filtered off, washed, dried, and cupelled with a little lead. The difference between the weight of crude platinum and of the residue from the treatment with aqua regia plus the weight of gold, gives the weight of platinum which has gone into solution.

The iridium is dissolved from the residue left on treatment with aqua regia, by heating with strong aqua regia; the final residue is only osmiridium.

The solutions obtained from gold-bearing ores are evaporated to dryness on the water-bath with addition of ammonium chloride, the ammonium platinic chloride extracted with absolute alcohol, to remove the ammonium auric chloride and the gold precipitated from the solution with ferrous sulphate, after removal of the alcohol and acidifying with hydrochloric acid.

The residue from the treatment with alcohol is dried, the ammonium chloride volatilised, the residue ignited, and the platinum dissolved out with weak aqua regia, and so on.

For the *Electrolytic Separation of Platinum*, cf. Classen, *Chemical Analysis by means of Electrolysis*, English translation, p. 276.

## PLATINUM ALLOYS

### 1. Platinum, Gold, and Copper.

The removal of copper is effected by cupelling with eight to thirty times the weight of lead, at a high temperature; the bead is then

<sup>1</sup> *Dingl. polyt. J.*, 1854, 133, 270.

<sup>2</sup> *School of Mines Quarterly* (Columbia University, New York), 17, 26; *Berg. u. Hütten. Zeit.*, 1896, 55, 235; *J. Soc. Chem. Ind.*, 1896, 15, 379.



flattened, treated with aqua regia, the platinum precipitated as ammonium platinum chloride, by evaporation with ammonium chloride, and the gold precipitated from the hydrochloric acid filtrate with ferrous sulphate.

## 2. Platinum, Silver, and Copper.

The alloy is cupelled with eight to thirty times its weight of lead and sufficient silver to give, in the resulting alloy, five parts of silver to one of platinum.<sup>1</sup> The approximate platinum content must be ascertained by a preliminary assay. The flattened bead is boiled for a quarter of an hour with concentrated sulphuric acid, and the resulting platinum powder similarly treated with dilute sulphuric acid, and finally with water. The residue is then transferred to a small crucible, as in the case of the gold powder in the gold assay. Any retained silver is determined by dissolving in aqua regia, evaporating, and filtering from platiniferous silver chloride, then dissolving the silver chloride in ammonia and reprecipitating it by acidifying with nitric acid.

## 3. Platinum, Silver, and Gold (with Copper and Osmiridium).

Two hundred mg. of the alloy are cupelled with eight to thirty times as much lead, sufficient silver being added to ensure a ratio of three parts of silver to one of gold in the resulting alloy; copper is determined by difference. The alloy is then flattened and rolled, with repeated annealing, the cornet boiled first with concentrated sulphuric acid, then with dilute sulphuric acid, and finally with water, after which it is dried, ignited, and weighed. The loss, less the amount of added silver, represents the silver in the 200 mg. of original alloy taken for the assay. The cornet is then cupelled with an excess of silver (at least twelve times the weight of the presumed, or approximately determined, platinum content) and assay lead, a fresh cornet made, and boiled first with nitric acid of sp. gr. 1.16, then with somewhat stronger acid of sp. gr. 1.26; the platinum and silver go into solution.<sup>2</sup>

On treatment of the residue, consisting of gold and osmiridium, with aqua regia, only gold goes into solution, and this is precipitated in the usual way.

A somewhat modified method is described by Oemischen.<sup>3</sup>

**Recovery of Platinum from Platinum Residues** obtained in potassium estimations; *cf.* Vol. I., p. 521.

<sup>1</sup> Riemsdijk, *Berg. u. Hütten Zeit.*, 1886, 45, 213.

<sup>2</sup> In regard to the solubility of platinum-silver alloys in nitric acid, *cf.* Gold Inquartation, p. 141.

<sup>3</sup> *Berg. u. Hütten. Zeit.*, 1901, 60, 137; *J. Soc. Chem. Ind.*, 1901, 20, 507.

## MERCURY

The most important ore of mercury is *Cinnabar*, which, in its purest form, contains, 86.21 per cent. of mercury; tiny drops of metallic mercury are occasionally found in it.

*Idrialite* is a peculiar variety of cinnabar from Idria; it is a mixture of cinnabar with idrialine (a hydrocarbon which is present in idrialite to the extent of as much as 75 per cent.), iron pyrites, clay, and gypsum. Hepatic cinnabar and the spathic iron ore of Idria contain cinnabar, idrialine, bitumen, and other carbonaceous substances, in very varying amounts.

Other mercury ores are *Calomel*, *Mercury selenide*, and the *Silver amalgams*, containing varying percentages of mercury, but they are not found in large quantities and do not call for commercial examination. As much as 17 per cent. of mercury occurs in some Hungarian and Tyrolese fahl ores.

The most frequently employed method of assaying mercury ores is the rapid gold amalgamation assay, due to Eschka; it gives satisfactory results. Distillation tests, in which the mercury is collected as such, are practically only used as works' tests. Purely analytical wet methods are very seldom used, though electrolytic methods are occasionally employed.

**Distillation Test for Mercury.**

Average samples, up to 2 kg. in weight, are mixed with from one-half to an equal weight of black flux, and heated to a bright red heat in earthenware or iron retorts or pipes, and the mercury is condensed by water-cooling.

H. Rose's<sup>1</sup> distillation method, carried out on a smaller scale, gives very good results. The mercury compounds (cinnabar, calomel, corrosive sublimate, sulphate, etc.) are decomposed with calcium oxide at a moderate temperature in a hard-glass combustion tube; the mercury vapour is driven out of the tube by means of carbon dioxide, and condensed by cooling. The method is carried out as follows:—

A layer of roughly powdered magnesite (which is better than either chalk or sodium bicarbonate), 25 to 50 mm. in length, is introduced into a combustion tube closed at one end and having a length of 30 to 45 cm., with a diameter of 10 to 15 mm.; a mixture of ore and burnt lime, and then a layer of lime and a loose plug of asbestos, are placed in front of the magnesite. The end of the tube is drawn out and bent downwards at an obtuse angle. By carefully tapping the tube, while it is held in a horizontal position, a channel is formed for the subsequent escape of the carbon dioxide. The tube

<sup>1</sup> Rose-Finkener, *Handbuch d. analytischen Chemie*, vol. ii., pp. 187 *et seq.*

is placed in a furnace, which slopes slightly, and is heated, first at the end where the free lime is contained, until it attains a red heat at this section; the mixture itself is then heated, and finally the magnesite. The drawn-out end of the tube dips under water, contained in a small flask, in which almost all the mercury is collected; the end of the tube is cut off, and the drops of mercury remaining therein are washed out and added to the bulk in the flask. In some cases an open combustion tube is used, coal gas being passed through during the distillation. The collected mercury is transferred to a tared porcelain crucible, the water poured off as completely as possible, and the remainder removed by absorption with filter paper, after which the crucible is placed for a short time in an air-bath (or better still for several hours in a desiccator over sulphuric acid), dried, and weighed.

This method must be used if the material under investigation contains notable quantities of mercury salts (chlorides, sulphates), as these latter volatilise partially undecomposed, if the otherwise satisfactory Eschka method be employed. Fahl ores containing mercury are distilled with their own weight of iron turnings in glass retorts. With roasted ores an equal weight of litharge is mixed, in addition.

### The Eschka Gold Amalgamation Assay.

This method has been especially worked out in Idria. A Meissen porcelain crucible is used in the assay, about 45 mm. deep, upper diameter 48 mm., lower 22 mm., and of 50 c.c. capacity; the edge must be true, and it must be provided with a well-fitting lid of gold (Fig. 51), weighing about 10 g., of the shape of the lid of a platinum crucible, but having a depth of from 6 to 8 mm.

According to C. Winkler, a lid of pure silver may be used, but, in the case of a very small mercury deposit, this cannot be detected with certainty.

Holloway uses a flat silver plate, and places a metal box, through which a stream of cold water is kept running, on the top of the plate.

The amount of ore to be taken for the assay depends on the richness in mercury: with ores containing up to 1 per cent., 10 g. should be taken; with 1.5 to 10 per cent. of mercury, 5 g.; with very rich ores, 0.5 to 2 g. suffice. The approximate value is ascertained by a preliminary assay, using 1 g. of material. The ore is mixed in the crucible with half its weight of iron filings, which must be absolutely free from oily impurities, a 5- to 10-mm. layer of iron filings put on the top, and the weighed gold

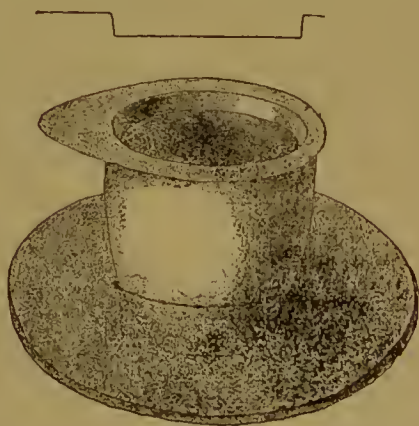


FIG. 51.



or silver lid placed in position and carefully pressed tight on to the crucible edge by means of a smooth metal plate; the lid is filled with distilled water, and the crucible bottom is then heated for ten to fifteen minutes by means of a gas or spirit flame. Pufahl places the crucible in an asbestos ring, which protects the upper part of the crucible and the lid from unnecessary heating. After cooling, the lid is removed, the water poured away, the lid washed on both sides with alcohol, dried on a watch-glass over a hot water-bath for two or three minutes and weighed after a quarter of an hour. The mercury is subsequently removed by heating the lid carefully over a small Bunsen flame, in a draught cupboard.

If too much ore be taken, the correspondingly large quantity of mercury deposited on the lid requires very careful washing. In such cases also the lid is affected by the excessive amount of mercury, and after volatilisation of the deposit, the surface remains rough and no longer fits accurately on the crucible; a preliminary assay should, therefore, always be made, if the mercury content of the ore is quite unknown.

Small losses of mercury, during the progress of the assay, are unavoidable. Balling states that in Idria the following corrections are added :—

Ore Value.	Correction.
Hg per cent.	Per cent.
Up to 0·4	0·04
0·4 to 0·7	0·06
0·7 „ 1	0·08
1 „ 3	0·15
3 „ 5	0·20
5 „ 10	0·25
10 „ 20	0·35
20 „ 30	0·45
30 and over	0·50

Bituminous ores, when decomposed by means of iron only, give tarry distillation products, which collect with the mercury and cannot be removed by merely washing. If red lead is added (Eschka), complete combustion of the bitumen is effected, but there is, at the same time, a slight volatilisation of lead, and also a superficial oxidation of the mercury.

To overcome this difficulty, the following modification of the Eschka process is employed in Idria :<sup>1</sup>—Rich and medium ores are mixed with well-ignited hammer-scale, which has been passed through a fine sieve; above this is placed a layer of hammer-scale, and, on top of all, oxide of zinc. Poorer ores are mixed with ignited barium carbonate, and the mixture is covered with hammer-scale and zinc oxide.

<sup>1</sup> Kroupa, *Berg. u. Hütten. Zeit.*, 1890, 49, 150.



For poor ores the weight taken is 10 g., for richer ores 2 g., for fume 0.5 g.; 10 g. of hammer-scale are mixed in with a glass rod, the mixture is covered with 10 g. of hammer-scale, and above this is added about 3 g. of zinc oxide.

R. Biewend<sup>1</sup> has considerably improved the Eschka assay. He advises that no more material shall be taken than will produce 0.2 g. of mercury. Instead of iron he uses copper filings; to aid in keeping back the heat from the gold amalgam, he recommends covering the mixture with calcined magnesia. The separation of the mercury is effected in two stages. The greater part is distilled off at the lowest possible temperature, then, after cooling, a second lid is put on and the crucible is heated to redness. To protect the lid from the heat of the flame, the crucible is placed in a hole cut in asbestos, as recommended by Pufahl. Biewend found that the loss, even in the case of pure cinnabar, did not exceed 0.2 per cent.

C. Ehrmann and J. Slaus-Kantschieder<sup>2</sup> have found that the Eschka method is not suited to pyritic ores. They assayed Dalmatian ores of this character by heating in a current of chlorine.<sup>3</sup>

### Amalgams.

The mercury in gold and silver amalgams is usually determined by distillation from glass or iron retorts, the gold or silver being subsequently cupelled and weighed, and the mercury ascertained by difference.

Copper amalgams, etc., used in dentistry are heated in a porcelain boat in a combustion tube in a current of hydrogen. About 1 g. of material is used, the tube is heated quite gradually to a red heat, and the mercury determined by loss.

A similar method is employed for white metals containing mercury (anti-friction metals).

### Electrolytic Methods of Estimation.

Several of these methods have been introduced in practice.

De Escosura<sup>4</sup> heats 0.5 g. of finely powdered ore in a porcelain dish with 10 to 15 c.c. of hydrochloric acid and 20 c.c. of water, 0.5 to 1 g. of potassium chlorate is added, a little at a time, and the heating continued until the cinnabar is completely dissolved; 50 c.c. of water are then added, and the free chlorine boiled off. Selenium and tellurium are precipitated by adding 20 c.c. of a saturated solution of ammonium sulphite and boiling for a few minutes; after standing for half an hour,

<sup>1</sup> *Berg. u. Hütten. Zeit.*, 1902, 61, 441; *Chem. Zeit.*, 1903, 27, 400.

<sup>2</sup> *Chem. Zeit.*, 1902, 26, 201; *J. Soc. Chem. Ind.*, 1902, 21, 501.

<sup>3</sup> Fresenius, *Quantitative Analysis*, 7th edition, vol. ii, p. 384.

<sup>4</sup> *Berg. u. Hütten. Zeit.*, 1886, 45, 329; *J. Chem. Soc. Abstr.*, 1886, 50, 650.

the precipitate is filtered off and washed until the filtrate amounts to about 200 c.c. The filtrate is electrolysed for twenty to thirty hours, using two Bunsen cells, a cathode of gold foil, and an anode of platinum foil; after the electrolysis is completed, the cathode is washed with alcohol, dried, and weighed. A number of assays can, of course, be carried out simultaneously by this method.

According to a more recent method of de Escosura's, the ore may be electrolysed without previous solution: 0.2 g. of 10 per cent. ore is treated cold in a platinum dish with 10 c.c. of hydrochloric acid, 90 c.c. of water, and 20 c.c. of a cold, saturated solution of ammonium sulphite. The dish serves as the anode, and a piece of gold foil is used as the cathode.

This method is a modification of that due to Classen,<sup>1</sup> who treats the ores with water acidified with hydrochloric acid, or with a 10 per cent. solution of common salt, and adds ammonium oxalate. The mercury is then deposited on a matte platinum cathode placed in the solution.

According to Classen, about 0.3 g. of mercury can be deposited completely from the ammonium oxalate solution at ordinary temperatures, in from two to three hours, with an E.M.F. of 4 to 4.75 volts and a current density of 0.93 to 1.02 ampères per 100 sq. cm. of cathode surface.

Edgar F. Smith deposits the mercury from a potassium cyanide solution. To the oxidised solution containing about 0.2 g. of mercury, about 0.25 to 2 g. of potassium cyanide are added, the solution diluted to 175 c.c. with water, and electrolysed. According to Classen, the current density to be employed in this case is 0.03 to 0.08 ampère per 100 sq. cm., and the E.M.F. 1.65 to 1.75 volts.

Brand<sup>2</sup> adds a slight excess of sodium pyrophosphate to the oxidised solution, dissolves the precipitate in aqueous ammonia or ammonium carbonate, and electrolyses with a current capable of producing 2 c.c. of electrolytic gas per minute; 1 g. of mercury can be deposited in five or six hours.

Rising and Lenker<sup>3</sup> dissolve cinnabar in a strong solution of hydrobromic acid, neutralise with sodium hydroxide, add potassium cyanide to the diluted solution (see E. F. Smith's method), and deposit the mercury on a platinum cathode by a very weak current.

Mercury may also be determined electrolytically by the use of a rotating anode with or without a mercury cathode<sup>4</sup> (*cf.* Copper, pp. 167, 168). With the rotating anode only, the whole of the metal in an electrolyte

<sup>1</sup> *Quantitative Chemical Analysis by Electrolysis*, English translation by Boltwood, p. 203.

<sup>2</sup> *Z. angew. Chem.*, 1891, 4, 202; *J. Chem. Soc. Abstr.*, 1890, 58, 294.  
*J. Amer. Chem. Soc.*, 1896, 18, 96.

<sup>4</sup> *Cf. Electro-analysis*, E. F. Smith, 1908.

containing 0.5 g. of mercury, as mercurous nitrate, and 1 c.c. of nitric acid, made up to 115 c.c., may be deposited in ten minutes with a current of 7 ampères at 7 volts, the anode rotating 700 times per minute.

According to M. Perkin,<sup>1</sup> the determination of mercury electrolytically with a gold cathode, or with a rotating silver electrode, gives high results, and he considers that the best results are obtained with a rotating anode and a mercury cathode.

### Examination of Mercury for Impurities.

If mercury, freed from fatty matter and dust by means of hot sodium hydroxide, does not exhibit a bright, convex surface, but fouls glass, and if about 1 c.c., shaken round in a large porcelain dish, leaves a tail of metal and shows dark-coloured streaks, it contains foreign metals, such as tin, lead, zinc, copper, bismuth, and cadmium.

To examine for such impurities about 20 g. are distilled in a glass retort until only about 1 g. remains, and the residue examined. After dissolving in hot nitric acid of sp. gr. 1.2, any meta-stannic acid is filtered off, after addition of water, the filtrate evaporated down with sulphuric acid to precipitate lead, and mercury, copper, and bismuth precipitated in the filtrate from the lead with sulphuretted hydrogen. Hot nitric acid dissolves the copper and bismuth from this precipitate; the presence of copper is shown by the blue colour obtained on the addition of excess of ammonia, and bismuth by the white precipitate of basic nitrate, obtained by boiling down the solution and then diluting with water. Zinc, cadmium, and iron can be detected in the filtrate from the precipitate obtained with sulphuretted hydrogen.

A method for the complete quantitative examination of mercury has been worked out by Fresenius.<sup>2</sup>

### The Purification of Mercury.

Mechanical impurities, such as dust, grease, etc., may be removed by allowing the mercury to trickle into a tall cylinder, filled with a hot dilute solution of sodium hydroxide. After washing with water it is dried by means of a towel in a large porcelain dish and poured through a perforated filter paper until only about 1 c.c. remains behind. If the impurities consist of dissolved metals (lead, zinc, copper, tin, etc.), the purification may be effected chemically, by treating with acids, etc.

Thorough shaking of impure mercury with a nitric acid solution of mercurous nitrate dissolves the foreign metals; a mixture of chromic acid and sulphuric acid is also satisfactory as a purifying agent.

The following method, due to R. Finkener, as modified by Ulex, is especially satisfactory:—About 5 kg. of impure mercury are thoroughly

<sup>1</sup> *Faraday Soc.*, 1909-10, 5, 45; *J. Soc. Chem. Ind.*, 1909, 28, 493.

<sup>2</sup> *Quantitative Analysis*, vol. ii., p. 379.



shaken in a strong, stoppered bottle of 2 litres capacity, with 250 c.c. of ordinary hydrochloric acid and 75 c.c. of a concentrated solution of ferric chloride. In the course of from three to six days, a subdivision of the mercury takes place into innumerable tiny globules, which are covered with a layer of mercurous chloride, and which, in consequence, do not run together. After treatment for several days, the contents of the bottle are washed into a large, strong porcelain dish of about 5 litres capacity and washed four times with 2 litres of hot water, acidified with hydrochloric acid, to remove lead chloride, etc., the washing being accompanied by thorough agitation. The dish is then placed on a heated water-bath, and a concentrated hydrochloric acid solution of 200 g. of fresh stannous chloride poured on to the mercury and the whole warmed and stirred, at the same time, with a porcelain spatula until the mercury has all run together; the mercury is then washed in the dish with running water, dried with clean towels, and filtered through a perforated filter paper.

The best method for freeing mercury from foreign metals is by distillation, the surface being covered with iron filings. The distillation is often carried out in vacuo; many forms of apparatus have been described for this purpose.<sup>1</sup>

## COPPER

Wet methods are almost exclusively employed in the assaying of cupreous materials such as ores, raw materials, the metal and its alloys. The dry methods are tedious and lengthy, and at the same time wanting in accuracy; reliable results are only obtainable in the assaying of ores containing native copper, as in the case of the products dealt with at the smelting works of Lake Superior.<sup>2</sup> Both in England and in America the dry assay is occasionally taken as a basis for sales; in Germany the wet methods only are recognised.

*The Cornish Dry Assay* should be considered as an adaptation of metallurgical processes on a very small scale, to determine the amount of copper the smelter may expect to extract, and also to indicate any special difficulties that are likely to be met with in the refining of the metal extracted, rather than as a method for the exact determination of the copper contents. The principal stages in this assay consist of—(1) the concentration of the copper in a regulus by fusion with suitable fluxes in a crucible; (2) the roasting of the regulus with a view to converting the sulphides into oxides; (3) the reduction of the copper oxide by fusion with suitable fluxes and reducing agents to obtain

<sup>1</sup> Cf. Hulett, *Z. physik. Chem.*, 1900, 33, 611; *J. Soc. Chem. Ind.*, 1900, 19, 128.

<sup>2</sup> Cf. "Fire-Assay for Copper," G. L. Heath, *J. Amer. Chem. Soc.*, 1902, 24, 699; *J. Chem. Soc. Abstr.*, 1902, 82, 698.



crude copper; and (4) the refining of the copper obtained. Low results are invariably obtained by this method, the margin being generally from 1 to 5 per cent., as compared with the wet assay.

There are many different methods of wet assay, gravimetric, volumetric, and colorimetric. Naturally, the method adopted will depend on the character of the material, the time required, and the accuracy demanded; also ores, intermediate and final products are assayed by very varying methods.

The materials requiring to be assayed include the following:—

### Copper Ores.

Ores.	Composition.	Copper content.
<i>Native Copper</i> , usually of a high degree of purity, occurring in large masses in the neighbourhood of Lake Superior, and in New Mexico and Chili.		
<i>Oxide Ores</i> :—		Per cent.
Ruby copper ore (cuprite) . . . . .	$\text{Cu}_2\text{O}$ . . . . .	88·8
Malachite . . . . .	$\text{CuCO}_3, \text{Cu}(\text{OH})_2$ . . . . .	57·4
Azurite . . . . .	$2\text{CuCO}_3, \text{Cu}(\text{OH})_2$ . . . . .	55·2
Chrysocolla . . . . .	a hydrated silicate . . . . .	35 to 40
Atacamite . . . . .	$\text{CuCl}_2, 3\text{Cu}(\text{OH})_2$ . . . . .	59·4
Phosphates, Arsenates, and Sulphates are also frequently met with.		
<i>Sulphide Ores</i> :—		
Copper pyrites . . . . .	$\text{CuFeS}_2$ . . . . .	34·6
Erubescite (bornite) . . . . .	approximately $\text{Cu}_3\text{FeS}_3$ . . . . .	42 to 70
Copper glance . . . . .	$\text{Cu}_2\text{S}$ . . . . .	79·9
Indigo copper . . . . .	$\text{CuS}$ . . . . .	65·5
Enargite . . . . .	$4\text{CuS}, \text{Cu}_2\text{S}, \text{As}_2\text{S}_3$ . . . . .	48·4
Fahl ores . . . . .	Sulpho-salts with $\text{As}_2\text{S}_3$ and $\text{Sb}_2\text{S}_3$ as sulpho-acids, and $\text{Cu}_2\text{S}, \text{Ag}_2\text{S}, \text{FeS}, \text{ZnS}, \text{HgS}$ as sulpho-bases.	

The arsenical fahl ores are rich in copper and poor in silver, whilst the antimonial fahl ores frequently contain a high percentage of silver; the copper content varies from 15 to 43 per cent., silver 0 to 35 per cent., mercury 0 to 18 per cent.

The chief source of copper is copper pyrites which occurs frequently in conjunction with lead and zinc ores, iron pyrites, stibnite, mispickel, etc.

**Copper Matte** (low grade and high grade).—This often requires to be assayed both in works and commercial laboratories. Copper mattes are complex mixtures of sulphides, and besides copper, silver, iron, lead, and zinc, they often contain small quantities of nickel, cobalt, tin, arsenic, antimony, etc.; in technical laboratories, as a rule, only the

copper, lead, and silver require to be determined. In its purest form copper matte approximates very closely to the formula  $\text{Cu}_2\text{S}$ .

**Copper Speiss.**—This contains copper, silver, iron, nickel, etc., combined chiefly with arsenic and antimony.

**Copper Slags.**—These, with the exception of refinery slags, are poor in copper.

**Black Copper** (Blister Copper).—This is impure furnace copper, containing up to 95 per cent. copper, usually with silver and a little gold; the other impurities consist of iron and sulphur, and usually lead, zinc, bismuth, nickel, arsenic, antimony, etc., in smaller or larger amounts.

**Cement Copper** (copper precipitate) is the impure metal precipitated from solution by means of iron.

**Tough Copper.**—This is refined marketable copper, and contains, as a rule, over 99 per cent. of copper, a little oxygen as cuprous oxide, frequently silver (up to 0.03 per cent.), minute quantities of the foreign metals found in blister copper, also traces of sulphur, and occasionally selenium and tellurium.

**Electrolytic Copper.**—This is almost chemically pure, but sometimes contains traces of bismuth, antimony, or arsenic.

**Alloys of Copper** contain very varying proportions of copper, tin, zinc, nickel, lead, etc.

**Copper residues**, copper scale, sweepings, etc.

**Sulphate liquors** and plating baths.

**Cupreous pyrites cinders** (burnt pyrites).

## A. GRAVIMETRIC METHODS OF ANALYSIS

In these methods the copper is either precipitated electrolytically as metal, or is converted into the sulphide or thiocyanate; the electrolytic method is the most widely used.<sup>1</sup>

### Solution of the Material.

Malachite, azurite, black oxide, phosphates and arsenates dissolve easily in either hot dilute sulphuric acid or in hydrochloric acid; cuprite is dissolved by dilute nitric acid. Sulphide ores, such as copper pyrites, bornite, copper glance, indigo copper, enargite, fahl ores, etc., and copper matte are very finely ground and heated with strong nitric acid, tartaric acid being added with fahl ores; or aqua regia (one volume nitric acid to two volumes hydrochloric acid) may be used. After all action has ceased, it is usual to add an excess of concentrated sulphuric acid and boil on the sand-bath until sulphuric acid fumes begin to be evolved.

Copper silicates and slags are decomposed by long-continued boiling

<sup>1</sup> The Swedish Assay, as modified by Kerl, is described in the German Edition, vol. ii., pp. 599-602.

with 50 per cent. sulphuric acid and a little nitric acid, or, more rapidly, by warming with dilute sulphuric acid and potassium fluoride in a platinum dish, followed by ignition, to decompose the fluorides.

Copper slags which have been properly chilled on taking the sample and crushed to pass a 100-mesh sieve, are completely soluble in dilute hydrochloric acid when the proportion of silica is below 40 per cent. Slag is, therefore, sampled at the furnace by dipping a small iron rod into it, and plunging the rod immediately into a bucket of water, or by catching some of the slag in an iron ladle and pouring it into water. To obtain a hydrochloric acid solution of these slags, boiling water is added to the weighed sample contained in a beaker and the whole stirred vigorously during the addition of the necessary hydrochloric acid in order to keep the slag in suspension. The stirring must be continued until there is no danger of gelatinised slag adhering to the bottom of the beaker; the solution should then be boiled for a few minutes (Bannister).

Blister copper and tough copper are dissolved in nitric acid; sweepings, etc., are treated as above with nitric acid or with aqua regia, after the organic matter has been burnt off. Copper alloys are dissolved or decomposed by nitric acid.

### 1. The Electrolytic Determination of Copper.<sup>1</sup>

In 1867 a prize was offered by the Mansfeld Ober-Berg. und Hüttendirection for a rapid and at the same time accurate method of determining copper in ores and furnace products, which was awarded to C. Luckow for his electrolytic method of estimation.<sup>2</sup> At the time of its introduction, it gave an impetus to the study of other electrolytic methods of analysis; it is still to be regarded as the best method for the determination of copper.

Luckow's method and the various modifications that have been subsequently proposed, depend on the quantitative precipitation of copper, as a coherent and pure metallic deposit, on a weighed platinum apparatus having the form of a cylinder, cone, dish, or crucible.

<sup>1</sup> An account of the methods for the electrolytic determination of copper is given in the following works on electrolytic analysis:—

*Quantitative Analyse durch Electrolyse*, A. Classen, 5th edition, 1908.

*Quantitative Chemical Analysis by Electrolysis*, A. Classen, translated by B. Boltwood, from the 4th German Edition, 1903.

*The Theory and Practice of Electrolytic Methods of Analysis*, B. Neumann, translated by J. B. C. Kershaw, 1898.

*Practical Methods of Electro-Chemistry*, F. M. Perkin, 1905.

*Electro-Analysis*, E. F. Smith, 1908.

*Analyse des Métaux par Électrolyse*, A. Hollard and L. Bertiaux, 1906.

The bibliography of the subject is given in the report of the British Association Committee on "Quantitative Analysis by means of Electrolysis," *British Association Reports*, 1895, p. 254.

<sup>2</sup> *Z. anal. Chem.*, 1869, 8, 23.

The chief methods of electrolytic deposition of the metal that are of practical importance and universally employed are those from acid nitrate or sulphate solutions.

The current required for the deposition can be obtained from galvanic elements, thermopiles or accumulators; the last are generally used when many electrolytic determinations have to be carried out daily, and are undoubtedly the most advantageous source of supply. Several methods have also been described for the adaptation of the electric light current for this work.

If ordinary galvanic cells are used for the electrolysis, Bunsen, Grove, Daniell, or Meidinger cells can be employed. With two Bunsen cells, 20 cm. in height, four determinations, from solutions each containing from 0.5 g. to 1.0 g. of copper, can be carried out simultaneously in from six to eight hours, provided the solutions are of approximately the same copper content and contain about equal amounts of free nitric acid.

In all cases both an ammeter and a voltmeter should be inserted in the circuit to determine the current and the E.M.F. respectively,

and adjustable resistances should be employed for the regulation of the current. The arrangement of the circuits with these necessary adjuncts has been described by Classen,<sup>1</sup> Neumann,<sup>1</sup> Perkin,<sup>1</sup> E. F. Smith,<sup>1</sup> Nissenson and Rust,<sup>2</sup> H. Marshall,<sup>3</sup> C. A. Kohn,<sup>4</sup> and others.

**Platinum Apparatus and Stands.** — Of the various forms of electrodes, those, as first used at the Mansfeld works, consist of a platinum foil cylindrical cathode, and a platinum wire anode, for small quantities of copper; for larger quantities of copper, a large

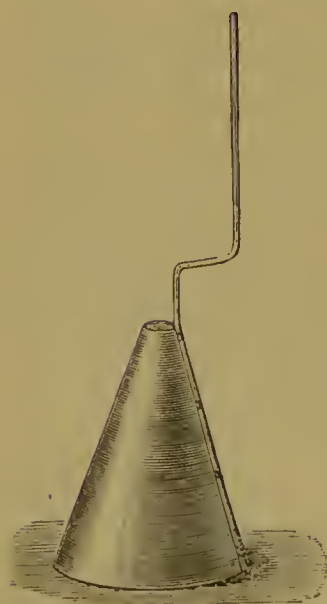


FIG. 52.



FIG. 53.

truncated cone (Fig. 52) is employed as cathode, with a positive electrode of the form shown in Fig. 53. Figs. 54 and 55 illustrate the arrangement of the electrodes.

<sup>1</sup> Cf. Literature, p. 159.

<sup>2</sup> *Z. anal. Chem.*, 1893, **32**, 429.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1900, **19**, 992.

<sup>4</sup> *British Association Reports*, 1896, p. 247.



Electrodes are also employed having the form of dishes, cups, cylinders, or spirals.

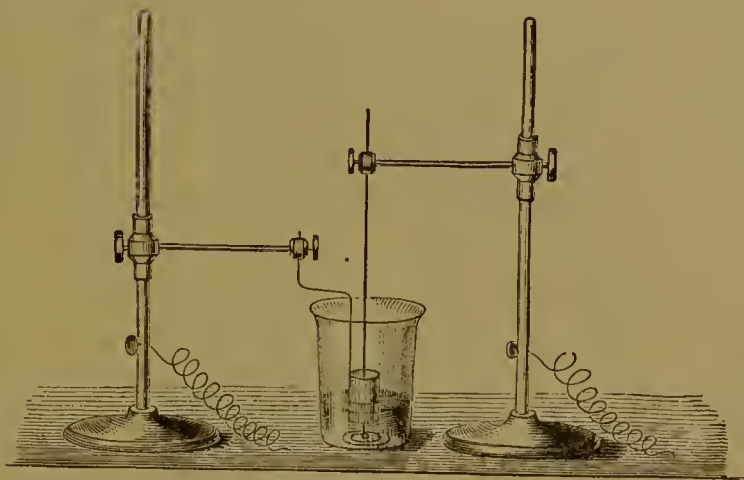


FIG. 54.

Both electrodes may be attached to an arm, which is divided at the middle by an insulating piece of vulcanite, or which consists of a thick glass rod.

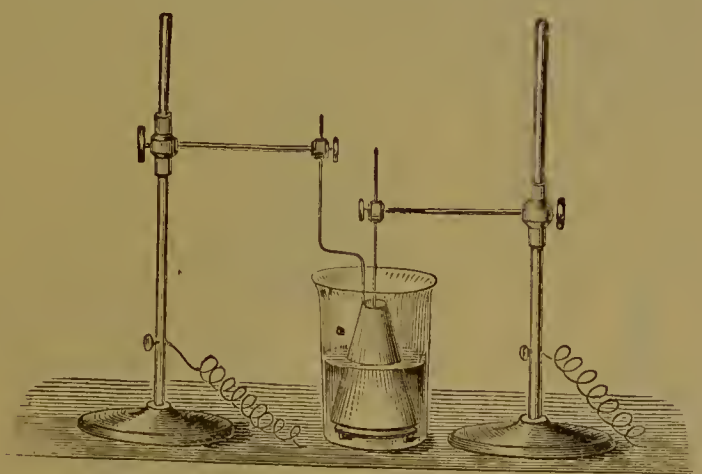


FIG. 55.

Using cylinder or cone cathodes, the electrolysis can be carried out in presence of insoluble material, such as gangue, etc., which remains at the bottom of the containing vessel; such cathodes are, therefore, especially suitable for the deposition of copper from the unfiltered solution obtained by boiling down the sample of ore with nitric acid and sulphuric acid, followed by treatment of the residue with water.

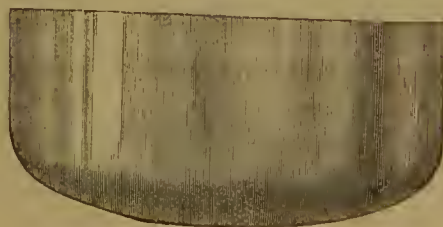


FIG. 56.

Classen's platinum dish cathode, Fig. 56, is stamped or hammered from platinum foil containing about 10 per cent. of iridium. It weighs

about 35 g., is 9 cm. in diameter, 4.2 cm. deep, and has a capacity of 250 c.c. The anode, Fig. 57, consists of a perforated platinum disc, 4.5 cm. in diameter, attached to a stout platinum wire. For the deposition of lead, as peroxide, a dish is employed which is roughened internally by sand blasting, as the lead peroxide adheres better to the roughened surface.

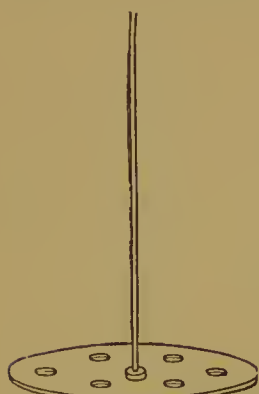


FIG. 57.

The dish, when in use, rests on three platinum contact points on the metal ring, shown in Fig. 58, and the anode is clipped at *e* in the upper support by means of a screw. The ring and support are capable of being adjusted on the thick glass stem *G* of the stand; *n* and *p* are the terminals. This arrangement allows of the contents of the dish being warmed by means of a small Bunsen flame, placed underneath; a piece of thin asbestos sheet, supported about 1 cm. below the dish, ensures equalisation of the heating.

Losses of liquid through spitting, due to the ascending gas bubbles, when using the cylindrical or conical cathode or the Classen dish, may be avoided by covering the containing vessel with the two halves of a divided

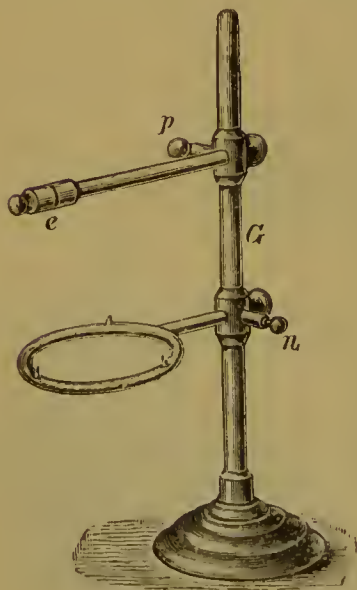


FIG. 58.

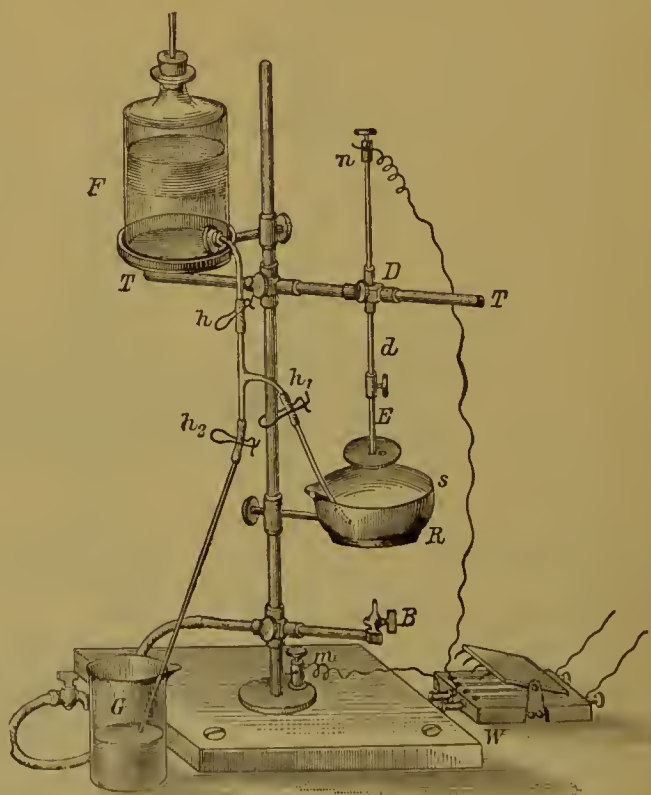


FIG. 59.

watch-glass, the edges being notched, by means of a small round file and turpentine, so as to take the wires of the cathode and anode.

Von Klobukow's "universal" stand (Fig. 59) is a great convenience, when working with a platinum dish.

R. Finkener's apparatus (Fig. 60) consists of a platinum crucible, weighing 60 to 70 g., and having a depth of 65 mm. with a maximum diameter of 60 mm. and a capacity of 150 c.c., provided with a watch-glass, perforated at the centre, a platinum spiral anode (or a piece of platinum foil with wire attached) and the necessary stand. The illustration shows the whole arrangement for the simultaneous carrying out of

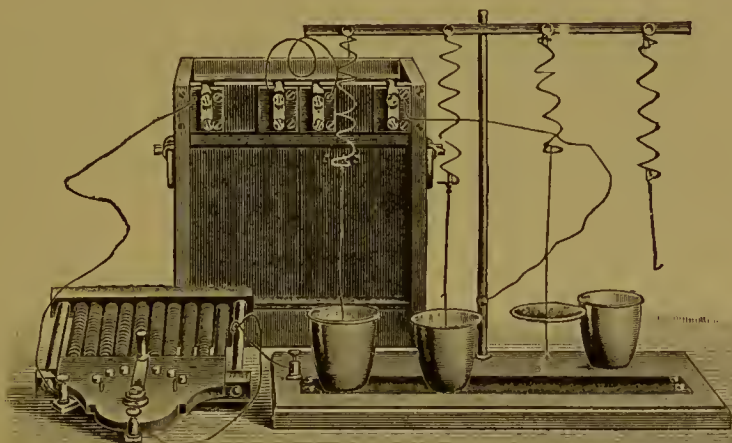


FIG. 60.

four depositions, viz., a two-cell accumulator, a German-silver 5-ohm. resistance, a stand of the form used by Pufahl, with a slate slab and gilded copper strips.

An improved form of stand has been devised by H. Marshall,<sup>1</sup> in which the conducting wires are attached to fixed terminal binding screws on a slate base; the terminals are in direct connection with separate parts of the supporting rod bearing the electrode arms.

**The Electrolysis.**—If other metals besides copper be present, the nitrate solution should not contain more than 10 per cent. of free nitric acid of sp. gr. 1.2; for pure copper solutions 3 per cent. suffices. Sulphate solutions should contain preferably from 3 to 5 per cent. of free sulphuric acid and 0.5 per cent. of free nitric acid of sp. gr. 1.2. If free nitric acid be not present, the copper is likely to be deposited in a spongy form, in which case it does not adhere satisfactorily to the cone, dish, or crucible, and loss consequently occurs on washing.

In analysing most copper alloys, after separation of tin and evaporation of the nitrate solution with sulphuric acid to precipitate lead, a sulphate solution is obtained, which is suitable not merely for the deposition of the copper, but also for the subsequent separation of the

<sup>1</sup> *J. Soc. Chem. Ind.*, 1898, 17, 227.



zinc or nickel. In such cases a large excess of nitric acid must be avoided, as this is converted, to a considerable extent, into ammonium nitrate, during the electrolysis. This salt interferes with the precipitation of nickel from the solution containing excess of ammonia, and also hinders the quantitative precipitation of zinc by sulphuretted hydrogen from the neutralised and diluted solution.

Gentle warming of copper solutions to about  $30^{\circ}$  aids the deposition very considerably.

The distance of the electrodes from each other should be 5 mm. in the case of weak solutions, and 10 mm. in the case of stronger solutions.

Using a current of from 1 to 1.5 ampères per 100 sq. cm. of cathode surface, and an E.M.F. of from 2.2 to 2.7 volts, the complete deposition of 1 g. of copper should occupy from six to seven hours; with a weaker current the deposition is correspondingly slower. A test must always be made after the electrolysis, to ascertain whether the deposition is complete. To do this, the solution in the beaker, dish, or crucible, as the case may be, is diluted by the addition of 10 to 20 c.c. of water, and the electrolysis continued for a further thirty to sixty minutes. If, during this time, no sign of copper is observable on that part of the cathode not previously covered by the liquid, the deposition may be considered complete, although traces of copper may still be present in solution. If the first test showed the electrolysis to be unfinished, this testing operation must be repeated; finally, several cubic centimetres of the liquid are removed with a pipette, and treated with sulphuretted hydrogen water in a test tube; there should be no brown coloration.

After complete deposition of the copper, the acid liquid is removed by means of a syphon and replaced with pure water until litmus paper indicates only a faintly acid reaction. The current is then switched off and the apparatus disconnected.

The cone or the cylinder is quickly immersed in a large beaker of water, then removed and given a second washing, placed on a filter paper for a minute or so to drain, and then dipped into a beaker of absolute alcohol and allowed to drain again on filter paper. The electrode is then dried by holding it for a minute or two in the warm air over a hot-plate or dish, allowed to stand for twenty to thirty minutes, and weighed. The electrode may be cleaned and made ready for another determination by immersing it in strong nitric acid. The weights of the cathodes should be checked periodically—say, once a fortnight.

If a dish is used as the cathode, it is removed from the stand, quickly washed three times successively with 10 to 20 c.c. of water, then once with 10 c.c. of absolute alcohol, and dried in an air-bath at  $90^{\circ}$  or on a water-bath. If the apparatus is rapidly disconnected in, say, a quarter of a minute, the syphoning off of the liquid referred to above and the



accompanying dilution may be dispensed with, for not more than a few tenths of a milligram of copper will dissolve in so short a time. This method of procedure is especially applicable when crucibles are used. The great advantage gained is that succeeding operations, such as the electrolytic separation of nickel, for example, can be effected without the necessity of first evaporating down the diluted solutions. The crucible is washed in the same way as the dish, dried, and weighed after standing half an hour; any liquid remaining on the anode is washed off and added to the main bulk. Previous to the electrolysis, cylinders and cones must be handled by the wire only, dishes and crucibles on the outside only, as otherwise any greasy matter from the skin may prevent the deposition of the copper on the parts touched.

**Influence of other Metals and Non-Metals on the Deposition of the Copper.**—*Zinc, Nickel, Cobalt*, and small quantities of *Iron* in the copper solution do not interfere; if much iron be present, the ferric salts, already in solution or formed during electrolysis, exert a solvent action on the deposited copper. In this case the solution must be considerably diluted, and an increased current density must be employed for the electrolysis; it is better, however, to first precipitate the copper with sulphuretted hydrogen or sodium thiosulphate from a sulphate solution, treat the copper sulphide with nitric acid until the separated sulphur is pure yellow, filter, and electrolyse the resulting copper solution.

*Lead* is usually removed as sulphate. Should it be present in the nitrate solution, it will be deposited, on electrolysis, on the anode, as the dark brown hydrated peroxide. If much lead be present, a roughened platinum dish is used as anode, and the copper is deposited on the platinum disc. In presence of sulphuric acid, some of this is retained by the lead peroxide.

*Manganese* is not deposited from solutions containing more than 3 per cent. of nitric acid, but gives only the violet coloration due to permanganic acid; from sulphate solutions it is precipitated as the dark brown hydrated peroxide, which only partially adheres to the anode and mainly floats in the liquid as a flocculent precipitate.

*Mercury* is deposited with the copper and is best removed by igniting or roasting the ore sample, etc., previous to solution.

*Silver* and *Bismuth* are also deposited with the copper, the former partially as peroxide on the anode. The silver is precipitated from the solution by adding the exact amount of sodium chloride solution necessary, the silver chloride being filtered off before electrolysis. The silver, however, remains as chloride with the insoluble matter on the filter paper, if the ore be first treated with aqua regia and then with sulphuric acid. Bismuth is subsequently determined in the deposited copper, by the method described on p. 199, and its amount deducted from that of the copper found.

*Tin* and practically the whole of the *Antimony* are removed in the initial treatment of the sample with nitric acid. Any tin that remains in solution forms a grey film after the copper has deposited. *Antimony* and *Arsenic* deposit to a slight extent with the copper, but the greater portion comes down as a black coating on the copper, after this is all deposited. Traces of arsenic and antimony produce peculiar black comma-like vertical streaks on the copper, and if much arsenic and antimony be present, they float as a black flocculent precipitate in the liquid.

When the deposited copper contains arsenic or antimony, or both, it is dissolved in nitric acid, the solution evaporated down to small bulk, so as to remove the excess of acid, diluted with water, excess of ammonia added, and the solution titrated with potassium cyanide (*cf.* p. 173). But, as the presence of much arsenic or antimony gives rise to high results in this case, it is better to remove them beforehand. This may be done in various ways. Should arsenic only be present, then, according to A. H. Low, 2 c.c. of a solution of 2 g. of sulphur in 10 c.c. of bromine are added to the chloride solution, which is then boiled, strong sulphuric acid added, and the whole evaporated to dryness. In presence of antimony, the fairly concentrated chloride solution is, according to Heath,<sup>1</sup> evaporated to a syrupy consistency with the solution of sulphur in bromine, and after a further addition of 20 c.c. of pure bromine, it is heated to nearly 300°, until antimonious bromide ceases to be given off. This method is particularly suitable for very impure blister-copper.

Arsenical and antimonial ores, copper speisses, etc., are very finely powdered and fused, in a covered porcelain crucible over a small Bunsen flame, with six times their weight of a mixture of equal parts of sulphur and anhydrous sodium carbonate, or six times their weight of anhydrous sodium thiosulphate; the heating is continued so long as sulphur is given off, the cooled melt extracted with boiling water, the residue washed with well-boiled hot water, containing a little ammonium sulphide, and then warmed with nitric acid, evaporated down with sulphuric acid, and so on.

Arsenic, antimony, and tin may also be separated from the impure copper sulphide precipitate by digestion with yellow sodium sulphide solution.

The treatment of ores, mattes, etc., with pure and dry chlorine in a bulb,<sup>2</sup> whereby sulphur, arsenic, antimony, tin, selenium, iron, bismuth, and some zinc and iron are volatilised as chlorides, is seldom carried out in practice, as usually only individual estimations are required, and not complete analyses of the materials.

#### Use of Rotating Electrodes for the rapid Electrolytic Deposition

<sup>1</sup> *Chem. Zeit. Rep.*, 1898, 22, 9.

<sup>2</sup> *Cf. Fresenius, Quantitative Analysis*, 7th edition, vol. ii., p. 384.

of Copper.<sup>1</sup>—Many methods have recently been devised for the rapid determination of copper by the use of strong currents, high voltage, and hot solutions, in conjunction with rapidly revolving electrodes, in order to obtain compact and adhesive deposits of the metal. In some cases the cathode is made to revolve, and in others the anode. When the latter method is used, the anode may consist either of a spiral wire arranged as shown in Fig. 61, or of a small dish, 7 cm. in diameter and 3 cm. deep, containing slits perpendicular to the edge and a circular opening in the bottom (Fig. 62); by this arrangement free circulation of the liquid is insured.

During the deposition of copper in a platinum dish cathode, the anode is made to revolve at a speed of from 600 to 700 revolutions per

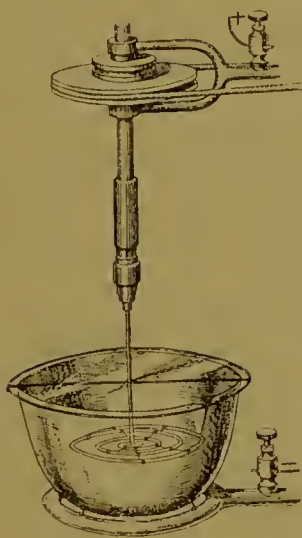


FIG. 61.

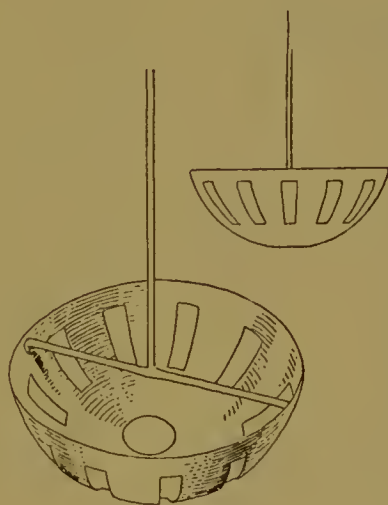


FIG. 62.

minute. A much more concentrated copper solution may be used than under the ordinary conditions of electrolysis, and it can be heated to near the boiling point. The electrolyte may consist of slightly acid sulphuric or nitric acid solutions, or of an ammoniacal or alkaline cyanide solution. In the acid solutions there should be about 1 c.c. of free sulphuric acid (1 : 10), or 0.5 c.c. of free nitric acid (1 : 1).

With sulphuric acid solutions, containing about 0.5 g. of copper diluted to 125 c.c., and heated nearly to boiling, the copper is deposited in about five minutes with a current of 10 to 15 ampères at a pressure of 8 volts.

For the determination of copper in pyrites, etc., it is often convenient to use an ammoniacal solution, and the following method may be adopted. The finely divided ore is decomposed with nitric acid, the

<sup>1</sup> Cf. *Electro-Analysis*, E. F. Smith, 1908, pp. 72 et seq.; *Electro-analytische Schnellmethoden*, A. Fischer, 1908; T. Slater Price, *J. Soc. Chem. Ind.*, 1909, 28, 117; H. J. S. Sand, *Faraday Soc.*, 1909, 5, 159.



solution evaporated to dryness, the residue moistened with a few drops of nitric acid and diluted with water; the resulting solution is then heated and filtered into a weighed platinum dish, where it is mixed with an excess of ammonium hydroxide. The iron present is thus precipitated as hydroxide, but may be left in the dish. The anode is put in motion and the solution electrolysed. The thorough agitation of the solution by the anode prevents any of the ferric hydroxide becoming attached to the deposited copper. In this case, with a dilution to 125 c.c., a current of 9 ampères, and a pressure of 8 volts, fifteen minutes are required for the deposition of about 0.5 g. of copper.

**Use of a Mercury Cathode with Rotating Anode, for the Electrolytic Deposition of Copper.**<sup>1</sup>—In this case a cup-shaped cell is used

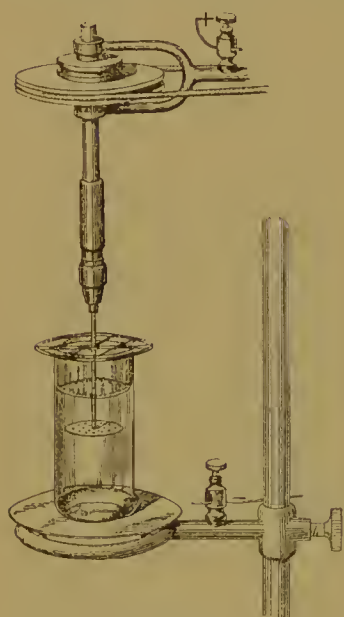


FIG. 63.

having a platinum wire fused through the bottom or the side near the bottom. Into this cup a layer of mercury is introduced sufficient to cover the platinum wire, and the whole is weighed. This cup is then placed on a plate of sheet copper connected with the negative electrode of a battery, the outside part of the platinum wire being in direct contact with the copper; by this means the mercury inside the cell becomes the cathode. The arrangement of the apparatus for an electrolytic deposition by this method is shown in Fig. 63.

The sulphate solution of copper, acidified with a few drops of sulphuric acid, is now introduced, and the revolving anode suspended from the rotator. The more concentrated the solution, the more rapidly will the copper be deposited, but the current should be continued several minutes after the solution becomes colourless, as the last traces of metal separate slowly. A current of about 5 ampères at a pressure of 6 volts should be used. When the metal has been completely deposited, the rotation of the anode is stopped, the cell filled with water, which is then syphoned off to the level of the anode and again filled up; this washing is continued until the wash water is free from acid. The wash water must always be tested for copper by means of sulphuretted hydrogen. The current is then interrupted and the amalgam thoroughly washed with water, then twice with absolute alcohol, and twice with ether. The cell containing the amalgam is then wiped dry on the outside, and, after the volatilisation of the ether, placed in a desiccator and subsequently weighed.

<sup>1</sup> Cf. *Electro-Analysis*, E. F. Smith, 1908, pp. 77 *et seq.*; T. Slater Price, *J. Soc. Chem. Ind.*, 1909, 28, 117.



## 2. Determination of Copper as Cuprous Sulphide (H. Rose).<sup>1</sup>

This method depends on the precipitation of the copper as sulphide from a warm, strongly acid solution of the sulphate or chloride by means of sulphuretted hydrogen. The voluminous greenish black precipitate is washed with water containing sulphuretted hydrogen and a trace of sulphuric acid, dried, the filter paper incinerated in a Rose's crucible, with subsequent addition of the copper sulphide and a few decigrams of sulphur, the whole gently and finally more strongly heated for twenty to thirty minutes in a current of pure dry hydrogen, allowed to cool in hydrogen, and the greyish black crystalline cuprous sulphide weighed; it contains 79.86 per cent. copper.

Hampe states that the weight of the cuprous sulphide should not exceed 0.2 to 0.3 g., as larger quantities of cupric sulphide cannot be completely converted into cuprous sulphide. Pufahl has, however, ascertained that 1 g. of copper can be converted into pure cuprous sulphide, provided that it is sufficiently strongly heated in hydrogen.

The method is particularly suitable for the separation of copper from solutions, which contain none of the metals precipitated by sulphuretted hydrogen from acid solutions (lead, bismuth, cadmium, arsenic, antimony, tin); also, it effects the separation of copper from zinc, nickel, cobalt, manganese, and iron.

Any mercury and arsenic which may be contained in the precipitate are volatilised during the ignition in hydrogen. If much arsenic be present, repeated heating with sulphur is necessary.

To carry out the determination, the dilute solution must be strongly acid, in order to ensure that zinc shall not be precipitated; 500 c.c. of the solution should contain preferably from 75 to 100 c.c. of free hydrochloric acid, or 10 c.c. of free sulphuric acid. The precipitation is effected in a covered beaker, which is kept warm, in a water-bath, at about 70°, and a rapid current of sulphuretted hydrogen is passed into the solution until the precipitation is complete. The precipitate is washed with very dilute sulphuretted hydrogen water, acidified with sulphuric acid; any hydrochloric acid remaining in the precipitate may cause a loss of copper, through volatilisation as chloride, during the subsequent heating.

As the process is tedious and takes up a considerable amount of time, it is seldom used for technical purposes, volumetric methods being preferred.

## 3. Precipitation of Copper with Sodium Thiosulphate.

The use of an aqueous solution of sodium thiosulphate as a substitute for sulphuretted hydrogen in qualitative analysis was first

<sup>1</sup> Cf. H. Rose, *Handbuch der analytischen Chemie*, 6th edition, by R. Finkener, p. 173. Fresenius, *Quantitative Analysis*, 7th edition, vol. i., p. 257.

recommended by G. Vortmann<sup>1</sup> and A. Orłowski,<sup>2</sup> and was subsequently introduced for the quantitative separation of copper by Vortmann and Orłowski, the copper being finally weighed as cuprous sulphide. Vortmann recommended its use also for the separation of copper from cadmium, which is not precipitated by sodium thiosulphate in acid solution. H. Nissenson and B. Neumann<sup>3</sup> have modified and considerably simplified the method by converting the cupric sulphide into copper oxide by roasting in a porcelain crucible.

The following is the procedure adopted by Nissenson and Neumann for the analysis of copper mattes and copper-lead mattes, which contain a considerable amount of iron and frequently zinc and arsenic, in addition to copper, lead, and sulphur. One gram of the finely powdered sample is dissolved by heating in an Erlenmeyer flask, on a sand-bath, with 7 to 10 c.c. of nitric acid of sp. gr. 1.4, and the solution, after addition of 10 c.c. of sulphuric acid, evaporated until white fumes of sulphuric acid are given off; the cooled residue is taken up with water, and silver precipitated by the addition of a few drops of hydrochloric acid. After thorough cooling, the lead sulphate, silica, and silver chloride are filtered off, washed with water containing 1 per cent. of sulphuric acid, and finally with distilled water. For the further treatment of the impure lead sulphate, *cf.* Lead, p. 222. The filtrate is boiled in a round-bottomed porcelain dish, with about 5 g. of sodium thiosulphate, until the copper sulphide settles well; this is then filtered off, washed well with hot water, the filter with precipitate transferred to a sufficiently large porcelain crucible, dried on the sand-bath, and the whole then placed in a moderately hot muffle; the temperature of the muffle must not be too high, as cupric oxide is partially converted into the suboxide at a high temperature.<sup>4</sup> The filter burns and the cupric sulphide is gradually converted into cupric oxide; any sulphate formed as an intermediate product loses its sulphuric acid completely on heating. After the first weighing, the crucible is again strongly heated in air, and this is repeated until a constant weight is attained. Any small quantities of tin, arsenic, and antimony, precipitated with the copper sulphide, are completely volatilised during the roasting in the muffle. The results obtained by Nissenson and Neumann, by this modified process, agree extremely well with those obtained by electro-deposition.

Tin and antimony, if present in the sample, are for the most part precipitated during the boiling with nitric acid, and are found in the lead sulphate; any portion of these metals that goes into solution is

<sup>1</sup> *Z. anal. Chem.*, 1881, 20, 416.

<sup>2</sup> *Ibid.*, 1882, 21, 215; *J. Chem. Soc. Abstr.*, 1882, 42, 1232.

<sup>3</sup> *Chem. Zeit.*, 1895, 19, 1591, 1592; *J. Chem. Soc. Abstr.*, 1896, 70, 450.

<sup>4</sup> *Cf.* Bailey and Hopkins, *J. Chem. Soc.*, 1890, 57, 269.

precipitated only to a small extent with the copper sulphide obtained by a not too lengthy boiling, and this volatilises with the arsenic, on heating in the muffle.

#### 4. Precipitation of Copper as Thiocyanate [ $\text{Cu}_2(\text{CNS})_2$ ] (Rivot's Method).

An aqueous solution of potassium or ammonium thiocyanate gives, with neutral or nearly neutral solutions of cuprous salts, a white precipitate with a tinge of violet, of cuprous thiocyanate; in the course of several hours the precipitation is complete. Zinc, cadmium, iron, nickel, cobalt, bismuth, tin, arsenic, and antimony are not precipitated, a circumstance which led Hampe<sup>1</sup> to introduce the method for the analysis of commercial copper. The cuprous thiocyanate is somewhat soluble in an excess of the precipitant, but only very slightly soluble in pure water.

To carry out the determination, the acid nitrate or sulphate solution of ore, furnace product, or alloy (brass, tombac, German silver, etc.), from which the lead and silver have been previously separated, is neutralised with sufficient sodium hydroxide to produce a permanent precipitate, and is then warmed to about  $40^\circ$  with a saturated aqueous solution of sulphur dioxide (30 to 50 c.c. per 0.5 g. of copper). Precipitation is then effected by the gradual addition of a solution of potassium thiocyanate of known strength. One cubic centimetre of a solution containing 76.5 g. potassium thiocyanate per litre will precipitate 0.05 g. of copper. Since cuprous thiocyanate is soluble to a certain extent in an excess of the precipitant, care must be taken to use the least possible excess. After standing for about four hours, the precipitate is collected on a good filter paper and washed with no more water than is absolutely necessary. If the filter paper has been previously dried at  $100^\circ$  to  $105^\circ$  and weighed, the weight of the copper thiocyanate can be ascertained after drying for four hours in an air-bath at  $100^\circ$  to  $105^\circ$ . It saves time, however, to convert the thiocyanate into cuprous sulphide. To effect this the filter and precipitate are dried rapidly, the filter burnt in a Rose's crucible, and the thiocyanate added and ignited; after cooling, an equal volume of sulphur is added, the whole gradually heated to redness in a current of hydrogen, then kept at a red heat for fifteen minutes, allowed to cool in hydrogen, and weighed.

In presence of much iron (as, for example, in the solution from copper pyrites), a blood-red coloration is at first produced on the addition of the thiocyanate; this gradually disappears through the action of the sulphur dioxide.

The metals mentioned above may be determined in the filtrate by first evaporating down, decomposing the slight excess of thiocyanate

<sup>1</sup> *Chem. Zeit.*, 1893, 17, 1691; *J. Soc. Chem. Ind.*, 1894, 13, 421.



by heating with nitric acid, and then following the usual analytical methods. Zinc, for instance, in the analysis of brass, is precipitated by adding excess of a dilute solution of sodium carbonate and boiling, the zinc being separated as basic carbonate.

Nickel and cobalt are precipitated by sodium hydroxide, boiled with addition of bromine water, and converted into the sesquioxides, which are washed for a short time, then dissolved in hot dilute sulphuric acid, with addition of aqueous sulphurous acid, the solution evaporated somewhat and treated with ammonia; the metals are then deposited electrolytically in a dish or crucible, or on a cone. This method is also employed in the analysis of nickel coins which contain 75 per cent. of copper and 25 per cent. of nickel.

In the case of German silver (copper, zinc, nickel), the zinc, after evaporation with excess of sulphuric acid, is precipitated from the very dilute and very slightly acid solution (about 500 c.c.) with sulphuretted hydrogen; after standing for twelve hours, the zinc sulphide is filtered off, washed with dilute sulphuretted hydrogen water containing a little ammonium sulphate, and dried; the precipitate is then heated with sulphur in a Rose's crucible in a current of hydrogen and the zinc weighed as sulphide. The nickel and cobalt are deposited together electrolytically in the filtrate from the zinc sulphide precipitate.

On account of the tardy quantitative precipitation of the thiocyanate and its appreciable solubility in water and in excess of potassium thiocyanate, this method is not so much used as the previously described gravimetric methods.

### 5. Precipitation of Copper with Ammonium "Cupferron." (Nitrosophenylhydroxylamine).

O. Baudisch<sup>1</sup> has proposed the use of the ammonium salt of nitrosophenylhydroxylamine,  $C_6H_5 \cdot N(NO) \cdot OH$ , under the name of "Cupferron," as a precipitant for copper, and as a means of separating it from nickel, cobalt, aluminium, and chromium. The method has also been investigated by H. Biltz and O. Hödtke.<sup>2</sup>

The reagent is employed in 6 per cent. aqueous solution, which can be kept for some weeks without material alteration, and which should be filtered if it has become turbid.

The precipitation is best carried out in acetic acid solution, or in mineral acid solution, mixed with the corresponding quantity of sodium acetate; any considerable quantity of free mineral acid dissolves the copper compound and prevents its quantitative separation. A considerable excess of the reagent, double the calculated quantity, is employed. Since the bright grey copper precipitate closely

<sup>1</sup> *Chem. Zeit.*, 1909, 33, 1298; *J. Soc. Chem. Ind.*, 1910, 29, 115.

<sup>2</sup> *Z. anorg. Chem.*, 1910, 66, 426; *J. Soc. Chem. Ind.*, 1910, 29, 721.



resembles the colour of the solid reagent, the completion of the precipitation cannot be clearly recognised until the precipitate has settled. The precipitate is filtered off on the pump, washed first with 1 per cent. sodium carbonate solution to remove the excess of the reagent, and then with water. The filter and the dried precipitate are carbonised in a covered crucible, and then ignited, with free access of air, or in a current of oxygen, to cupric oxide. The separation of copper from zinc is effected in acetic acid solution (1 atom Cu to 10 atoms Zn), that from cadmium (in the same proportions) only in mineral acid solution. The copper precipitate is first washed with faintly acidified water, then with 1 per cent. sodium carbonate solution, and finally with water. In the separation from zinc (copper used 0.1395 g.) the differences were + 0.4 and + 0.7 mg.; in the separation from cadmium (copper as above) the differences were + 0.5 and - 0.1.

The method is also applicable to the separation of copper from iron, as well as to the estimation of the latter metal, and to separating it from nickel, cobalt, aluminium, and chromium.<sup>1</sup>

## B. VOLUMETRIC METHODS OF ANALYSIS

Of the many volumetric methods devised for the estimation of copper, only those will be described that are much used in practice.

### 1. Parkes' Potassium Cyanide Method.<sup>2</sup>

This method is based on the decolorisation of blue ammoniacal cupric solutions by potassium cyanide with the formation of colourless, soluble potassium cuprous cyanides.

The potassium cyanide solution is prepared by dissolving 20 g. of the purest commercial potassium cyanide in 1 litre of water. It is standardised by a cupric solution containing 0.2 g. of copper dissolved in 5 c.c. of pure nitric acid, and diluted to 200 c.c., to which solution 20 c.c. of ammonia (1:1) are added. For the standardisation, the cyanide solution is run from a burette into the copper solution, contained in a flask, until the solution assumes a faint violet tinge, the solution having been kept stirred during the addition of the cyanide; after standing for a couple of minutes, complete decolorisation is attained.

Satisfactory results can only be obtained if all titrations are carried out under similar conditions as to temperature, time occupied, and the amount of copper, ammonia, and ammonium salts present.

<sup>1</sup> Cf. O. Baudisch and H. Biltz and O. Hüdtkke, *loc. cit.*; also, H. Nissenson, *Z. angew. Chem.*, 1910, 23, 629.

<sup>2</sup> Cf. Balling, *Probierkunde*, 1879, p. 274, where calculation tables are given.

Nickel and cobalt must not be present, on account of the colour of their ammoniacal solutions. Manganese must be previously removed by warming the ammoniacal solution, after addition of a little hydrogen peroxide. Zinc, if over 4 per cent., causes the results to come too high, and consequently makes the assay valueless. Arsenic and antimony should not be present to a greater extent than about 0.5 per cent. Lead and silver must be previously removed, and calcium, in large quantity, interferes with the results.

The process is used chiefly for the estimation of copper in ores and copper mattes, and is sufficiently accurate for ordinary smelter or mine work, but it is not recommended as the basis for regulating sales of cupreous materials. In controlling the sale price of ores, mattes, etc., either the electrolytic or the iodide method is almost invariably used.

The precise manner of carrying out the method varies with the nature of the ore. For pure or known materials, it is conducted as follows:—From 0.5 to 1 g. of the finely powdered material is weighed into a small flask and decomposed with 10 c.c. of nitric acid; in some cases a little hydrochloric acid may also be used. When thoroughly decomposed, a little water is added, then ammonia until neutral, and an excess of 20 c.c. of ammonia (1 : 1). The whole is diluted to 200 c.c., cooled in running water, and then titrated with the cyanide solution to complete decolorisation. In many cases the ferric hydroxide may be left in the solution and allowed to settle after each addition of cyanide, but in case it interferes with the end-point, it may be filtered off when only a faint blue coloration remains in the solution. Many prefer to filter off the iron before commencing the titration, but in this case the precipitate must always be redissolved and reprecipitated, the second filtrate being added to the first, as the ferric hydroxide invariably carries down some copper.

In the case of impure or unknown materials, the copper must be separated before titration. This may be effected either by means of sodium thiosulphate or of metallic aluminium. The former method is described on p. 169. The precipitate of copper sulphide is dissolved in nitric acid, neutralised with ammonia, and proceeded with exactly as described above.

The method of separation on metallic aluminium is very largely used, both for the cyanide method of assay and also for the iodide method, to be described later (p. 175). In this case, after decomposing the sample with nitric acid, 10 c.c. of sulphuric acid are added, and the whole heated until dense white fumes of sulphuric acid have been evolved for some minutes. The solution is then cooled, diluted to 50 c.c., a bent piece of aluminium foil,  $\frac{1}{16}$  in. thick and about 1 in. by 3 in. in size, added, and the whole boiled briskly until all the copper is precipitated. The whole of the copper should come down in from five

to ten minutes, and should not adhere to the aluminium; this only occurs if the piece has become pitted by being used a number of times. The aluminium is removed and washed, and the precipitated copper washed by decantation several times. It is then dissolved in nitric acid, the solution made alkaline with ammonia, and titrated as above. After separation on aluminium, the residual solution should always be tested for copper by means of sulphuretted hydrogen.

## 2. De Haen's Iodide method, as modified by Low.

The de Haen<sup>1</sup> iodide method for the estimation of copper, as modified by Low,<sup>2</sup> is widely used commercially, both in England and in America. Low is of opinion that it is better than the electrolytic method, as regards both accuracy and rapidity.

The determination is carried out as follows:—A solution of sodium thiosulphate, containing 38 g. of pure thiosulphate to the litre, is standardised with copper. One-fifth gram of chemically pure copper is dissolved in 4 c.c. of concentrated nitric acid in a flask of about 250 c.c. capacity, the solution boiled down to 1 or 2 c.c., 5 c.c. of water added, then 5 c.c. of strong ammonia, and the whole boiled for a minute. The boiling is absolutely necessary, as otherwise the liquid reacts with potassium iodide as though it contained free nitric acid. Six cubic centimetres of acetic acid are then added and 40 c.c. of cold water; the solution is thoroughly cooled, 3 g. of potassium iodide added, and allowed to dissolve.

The reaction is represented by the following equation; cuprous iodide is precipitated and iodine liberated:—



The thiosulphate solution is run into the copper solution containing the liberated iodine from a burette until the colour is only pale yellow, when starch solution is added until blue; the titration is then continued to decolorisation in the usual manner (*cf.* Vol. I., p. 117).

The starch solution must be made fresh every two days, by agitating 0.5 g. of starch with 250 c.c. of cold water, and then heating to boiling. The thiosulphate solution, made by dissolving pure sodium thiosulphate in pure boiled water, free from air, keeps for a month without change (*cf.* Vol. I., p. 121).

Low adopts the following method in the case of ores:—One gram of the finely powdered sample is treated with 10 c.c. of concentrated nitric acid, in a flask of about 250 c.c. capacity; the resulting solution is

<sup>1</sup> *Ann. Chem. Pharm.*, 1873, **91**, 237. The method was first described by E. O. Brown, *Quart. J. Chem. Soc.*, 1857, **10**, 65.

<sup>2</sup> *Eng. and Min. J.*, 1895, **59**, 124; *J. Soc. Chem. Ind.*, 1895, **14**, 304; *cf.* also, Westmoreland, *J. Soc. Chem. Ind.*, 1886, **5**, 48.



evaporated nearly to dryness, and the residue boiled for two or three minutes with 10 c.c. of concentrated hydrochloric acid; 10 c.c. of concentrated sulphuric acid are then added, and the boiling continued until fumes of sulphuric acid are evolved.

The cooled residue is treated with 10 c.c. of water, boiled and filtered from lead sulphate, gangue, sulphur, etc., into a shallow beaker of 8 cm. diameter. On the bottom of the beaker is placed a strip of thick aluminium foil, about 4 cm. wide and 7 cm. long, bent at the ends to prevent complete contact of the surface with the bottom of the beaker; the aluminium, which must be free from copper, may be used for a number of estimations. The volume of the filtrate and wash-water should be kept below 75 c.c. The beaker is covered with a clock-glass and the solution boiled well with the aluminium for six or seven minutes; the precipitation of copper should then be complete, though more dilute solutions require longer boiling. The solution, and, as far as possible, all the precipitated copper, washed off the aluminium by means of a wash-bottle, are transferred to the flask first used, the beaker for the time being put on one side; the solution is then decanted from the flask through a small filter and the contents of the flask washed three times successively by decantation with a very little hot water. The funnel, together with the filter, is then placed over the beaker, and 3 or 4 c.c. of strong nitric acid are dropped on, followed by a washing with a little hot water; this acid solution, which is also used to remove traces of copper remaining on the aluminium, is washed into the flask to the main bulk of precipitated copper, which is dissolved by heating over the free flame; 0.5 g. of potassium chlorate is added to oxidise any arsenic to arsenic acid, and the liquid boiled down to 1 to 2 c.c.; no basic salts of copper should separate during this concentration. The titration is then carried out as in the case of the standardisation described above.

Since 1 g. of pure copper requires 5.22 g. of potassium iodide, 3 g. of potassium iodide will suffice for 1 g. of all ores containing less than 50 per cent. of copper. For very rich ores, 5 g. of potassium iodide should be used.

Arsenic, as arsenic acid, does not interfere with the estimation; bismuth, by reason of the deep yellow colour of potassium-bismuth iodide, hinders the titration, and may cause the addition of starch to be made at too late a stage, though this does not frequently happen. Lead also masks the end-point to a certain extent; ferric salts must be absent.

Instead of neutralising with ammonia, as described in Low's method, many chemists prefer to use sodium carbonate. This should be added in very slight excess only, followed by the addition of acetic acid. If a large excess of sodium carbonate be used, the sodium acetate formed



interferes to a certain extent with the titration. Powdered marble is an advantageous reagent to use for the neutralisation, as an excess does not interfere. Another method which is much used is to add an excess of zinc acetate to the nitric acid solution, by which means zinc nitrate is formed and acetic acid liberated. This is found to be a very quick, clean, and reliable method of treatment.

The iodide method gives results which agree very closely with the electrolytic assay. It is used especially for controlling the sales of copper ores, mattes, etc.

### 3. Stannous Chloride Method. (F. Weyl.)<sup>1</sup>

This method is based on the reduction of cupric to cuprous chloride by stannous chloride. A hydrochloric acid solution of stannous chloride is added to the hot, deep green hydrochloric acid solution, containing cupric chloride and free from oxidising or reducing agents, until the green colour has disappeared. One drop of a concentrated solution of mercuric chloride should produce a very faint precipitate of mercurous chloride when the titration is finished. The end-point corresponds with the complete decolorisation of the liquid, and in a good light it is quite sharp. Balling,<sup>2</sup> who has examined the method very carefully, found the differences between results given by it and by gravimetric methods not to exceed 0.1 to 0.2 per cent.

The stannous chloride solution is prepared by dissolving 6 g. of pure tin, or the corresponding quantity of freshly prepared commercial stannous chloride, in 200 c.c. of pure 25 per cent. hydrochloric acid, and diluting to a litre with cold, boiled water. It is kept in quantities of 3 litres or more in a stock bottle connected with a small carbon dioxide generator to prevent oxidation.

A copper solution of known strength is prepared by weighing out exactly 7.854 g. of freshly prepared sulphate of copper, in small crystals previously dried by pressing between filter paper; this is dissolved in water and made up to 500 c.c. The solution contains exactly 2 g. of copper. Instead of using sulphate of copper, 2 g. of electrolytic copper may be dissolved in 8 c.c. of nitric acid of sp. gr. 1.4, the solution evaporated with 2 c.c. of sulphuric acid to completely remove nitric acid, the residue taken up with water, and made up to 500 c.c.

To standardise the stannous chloride solution, 25 c.c. of the copper solution, corresponding to 0.1 g. of copper, are run into a flask of 200 c.c. capacity, 5 c.c. of pure concentrated hydrochloric acid added, and the mixture brought to the boil, when stannous chloride solution is run in, from a freshly filled burette, until the green colour of the

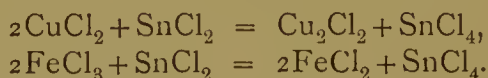
<sup>1</sup> *Z. anal. Chem.*, 1870, 9, 297; cf. also, *Chem. News*, 1873, 23, 49; 1884, 46, 284.

<sup>2</sup> *Die Probierkunde*, 1879, pp. 265 *et seq.*; tables for the calculation of the copper content are given on pp. 270 *et seq.*

boiling solution is discharged. Any greenish tinge appearing on the addition of a further 5 c.c. of concentrated hydrochloric acid will be discharged by one drop, or, at any rate, by a very few drops of stannous chloride solution. The stannous chloride solution must be re-standardised about once a week by means of the copper solution, which must be kept for the purpose in a tightly stoppered bottle.

The copper in ores is determined as follows:—From 2 to 5 g. of the finely powdered sample, according to its richness in copper, are boiled in a flask with aqua regia, and then evaporated nearly to dryness with sulphuric acid. On taking up with water and filtering, gangue, lead sulphate, and silver chloride remain on the filter paper; the filtrate is diluted to 250 c.c., of which 25 c.c. are run into a flask and treated with 5 c.c. of concentrated hydrochloric acid, etc., as above.

In presence of iron, as is almost always the case, the hydrochloric acid solution is of a yellowish green colour, and the stannous chloride used corresponds to the total of copper and iron. To determine the iron, a separate portion of 25 c.c. of the sulphate solution is warmed with granulated zinc, the clear solution poured off from the precipitated copper, the copper washed by decantation with water, and the combined solutions, after cooling, titrated with potassium permanganate. The same quantity of stannous chloride is required for 55.85 parts of iron as for 63.57 parts of copper, in accordance with the following equations:—



For the subsequent estimation of the copper, it is better to completely dissolve the excess of zinc (which must be free from lead) by warming with dilute sulphuric acid, decant, then add a sufficiency of nitric acid to dissolve the copper, boil down with sulphuric acid to remove nitric acid, dissolve in water, add hydrochloric acid, and titrate as above.

Any antimonious acid or antimony chloride in solution is reduced by the stannous chloride to antimonious chloride, and thus causes the copper to come out too high. This error may be estimated by allowing the titrated solution to stand for from twelve to twenty-four hours in an open dish, and then titrating again. During the exposure, the cuprous chloride is oxidised to cupric chloride, but the antimonious chloride remains unchanged. The second titration, therefore, gives the correct copper content.

Arsenic has no effect on the assay. Nickel and cobalt must be previously removed; this is most simply done by precipitating the copper with sodium thiosulphate (p. 169), treating the sulphide with nitric acid and sulphuric acid, and then titrating the sulphate solution in presence of hydrochloric acid.

The process is frequently used, especially where a stannous chloride solution is also used for the titration of iron.

#### 4. Ammonium Thiocyanate Method. (Volhard.)

This method consists in the precipitation of the copper as cuprous thiocyanate from a nearly neutral hot solution, saturated with sulphur dioxide (*cf.* also, p. 171). The precipitation is effected by a slight excess of a measured solution of ammonium thiocyanate of known strength, the excess being titrated back, in the cold, with silver nitrate solution, in presence of ferric sulphate and nitric acid.

Any silver, mercury, chlorine, bromine, iodine, and cyanogen must be previously removed.

To carry out the estimation, the nitric acid or sulphuric acid solution of the sample is first nearly neutralised with sodium carbonate or sodium hydroxide, free from chlorine; for about 0.5 g. of copper, approximately 50 c.c. of a saturated aqueous solution of sulphur dioxide are then added, the whole heated to boiling and precipitated with an excess of an ammonium thiocyanate solution standardised by silver nitrate (*cf.* Vol. I., p. 123). (As 107.88 parts of silver require the same amount of ammonium thiocyanate for precipitation as 63.57 parts of copper, the silver titre must be multiplied by  $\frac{63.57}{107.88} = 0.5893$ .)

It is convenient to use a 500 c.c. flask for these operations, or else to wash the total liquid, after cooling to the ordinary temperature, into a flask of this size, and to dilute to the mark, mix, allow to stand for a short time, and then filter an aliquot portion through a dry filter paper into a dry beaker.

One hundred cubic centimetres of the filtrate are then treated with 5 c.c. of a cold saturated solution of iron alum and a few drops of pure nitric acid, and the solution titrated with a standardised silver nitrate solution, until the ferric thiocyanate colour is discharged. The amount of thiocyanate used for the precipitation of the copper is thus obtained.

The estimation of copper in blister copper, alloys, mattes, and ores, the copper content of which is approximately known, can be carried out in a short time by this method, and the results are sufficiently accurate for technical purposes. The error introduced by not taking account of the volume of the solid cuprous thiocyanate is negligible.

#### C. COLORIMETRIC METHODS

The object of these methods is the determination of the copper content of definite volumes of blue ammoniacal cupric solutions by comparison with the colour of standard solutions containing known quantities of copper, in layers of similar thickness and of equal volume.



As in all colorimetric methods, it is taken for granted that the colour intensity of equal columns of solution is directly proportional to the amount of colour-producing material in the liquid.

The colorimetric determination of copper was originally recommended by Jacquelin, von Hubert, and others for rich as well as poor ores, graduated tubes being employed, such as are used in the Eggertz colorimetric estimation of carbon in steel (*cf.* p. 57); the method is now only employed, in Heine's modified form, for the assay of poor ores, furnace products, and slags, the copper content of which does not exceed 1 per cent.

Strongly coloured solutions are very difficult to compare; if such solutions be considerably diluted to many times the normal volume and the content then ascertained by comparison with the standard solution, it is necessary, of course, to multiply by the dilution factor, and so the experimental error becomes increased to a corresponding degree.

An ammoniacal solution, prepared from the ore with nitric acid, must be compared with a standard solution prepared from copper nitrate, and a solution made with sulphuric acid must be compared with a copper sulphate solution, the colours of the ammoniacal solutions of these two salts being somewhat different.

The solutions to be compared must be at the same temperature, and must contain equal amounts of ammonia; they must be prepared with good distilled water, quite free from organic matter, and with similarly pure ammonia, otherwise a greenish coloration results. Bituminous ores must be roasted to decompose organic matter before being treated with acids.

Nickel and cobalt interfere with the estimation, as does also arsenate of iron, which gives a brown coloration with ammonia; small quantities of nickel give a violet tinge to the solution, and such a solution is difficult to compare with the pure blue solution of pure copper. These impurities may be removed by previous precipitation of the copper as sulphide, which is then dissolved in nitric acid; it is advisable also to precipitate the copper as sulphide from solutions containing much iron and aluminium, as the bulky precipitates of the hydroxides of these metals retain copper tenaciously.

#### Heine's Method for Low-grade Ores and Slags.

Solutions of nitrate or sulphate of copper, containing exactly 1 mg. of copper per cubic centimetre, are made by dissolving electrolytic copper; quantities of 20, 10, 7.5, 5, 4, 3, 2, 1 c.c. are taken out with pipettes and put into measuring flasks or cylinders; after adding 10 c.c. of pure ammonia to each, they are diluted to 100 c.c. and placed in perfectly similar, square glass-stoppered bottles of about 150 c.c. capacity. The bottles are labelled as 2, 1, 0.75, 0.5, 0.4, 0.3,



0.2, 0.1 per cent.; the stoppers are fastened down with parchment paper caps.

To carry out an estimation, 2 g. of an ore, such as Mansfeld "Kupferschiefer," are roasted in a porcelain crucible in a muffle and then treated in a beaker with 15 c.c. of a mixture of three parts of sulphuric acid of sp. gr. 1.26, and one part of nitric acid of sp. gr. 1.2, and the whole boiled down on a sand-bath until sulphuric acid fumes are evolved. On cooling, the mass is taken up with distilled water, and the volume made up to 100 c.c. in a graduated flask, 30 c.c. of strong pure ammonia added, and the whole well mixed and filtered into the sample bottle, marked for 200 c.c. After thorough cooling, the solution is diluted to the mark and the bottle placed between the standard bottles, at a window, in front of a screen covered with white paper. On account of the constant amount of nickel in the "Kupferschiefer," the standard solutions are made up with the necessary amount of nickel by the addition of a solution of electrolytic nickel. If the colour of the ammoniacal solution from 2 g. of ore, diluted to 200 c.c., agrees with the standard solution of 20 mg. of copper in 100 c.c., it follows that the ore contains 2 per cent. of copper; should the colour be deeper than that of the strongest standard, the assay solution is diluted to twice its volume and a sample bottle filled with the diluted solution, comparisons being again made, and so on.

According to Heath,<sup>1</sup> slags at the works at Lake Superior are usually assayed colorimetrically, as follows:—Two and a half grams of finely powdered slag are boiled in a porcelain dish with concentrated nitric acid (sp. gr. 1.4), until all nitrous fumes are driven off, 10 c.c. of sulphuric acid then added, and the boiling continued until the mass is pasty. After taking up with water and adding excess of ammonia, the solution is filtered on the pump into a 200 c.c. graduated bottle and the precipitate washed with very dilute ammonia (1 to 10); the cooled solution is then made up to 200 c.c. and the test carried out as described with suitable standards.

J. D. Audley Smith<sup>2</sup> uses only one solution for the comparison containing 2.5 mg. of copper per cubic centimetre. The solution under examination is placed in a 200 c.c. bottle; 150 c.c. of water are placed in a similar bottle, the same amount of nitric acid and of sulphuric acid as in the case of the sample, and 30 c.c. of ammonia (sp. gr. 0.9), added, and a copper solution of known strength then run in from a burette until a corresponding colour is produced.

Refractory slags are best fused with potassium fluoride and sulphuric acid in a platinum dish, the melt dissolved, the iron oxidised with nitric acid, and the solution then evaporated down until fumes of

<sup>1</sup> *Eng. and Min. J.*, 1895, 59, 369, 370; *J. Soc. Chem. Ind.*, 1895, 14, 679.

<sup>2</sup> *Trans. Amer. Inst. Min. Eng.*, Canadian Meeting, 1900; *Chem. Zeit. Rep.*, 1900, 24, 291.

sulphuric acid are evolved; the colorimetric comparison is then made as above.

For the estimation of small quantities of copper in litharge, 10 g. or more of the sample are treated with dilute nitric acid, evaporated down with sulphuric acid, 50 c.c. of water added, and the solution filtered into a graduated flask of 100 c.c. or other agreed standard capacity.

Waller<sup>1</sup> gives the following excellent method for the colorimetric estimation of copper in slags:—Two grams of the slag are placed in a small beaker, 50 c.c. of hot water and then 15 c.c. of hydrochloric acid added at once while the slag is kept in suspension by vigorous stirring. Practically all the silica, lime, oxide of iron, etc., is dissolved, and can be filtered off from the black residue, which consists of copper sulphide and a little, partly decomposed, slag and matte. The solution always smells strongly of sulphuretted hydrogen, which ensures the copper remaining insoluble. The residue is filtered off on the pump, as otherwise the filtration is slow owing to a slight separation of gelatinous silica, which often occurs. The filter paper is ignited in a porcelain crucible, no organic matter being allowed to remain, the residue brushed into a beaker, 5 c.c. of nitric acid and a few drops of hydrochloric acid added, and heated till red fumes cease to come off. The resulting solution is then diluted, 20 c.c. of ammonia added, the solution boiled, filtered into a colorimetric bottle, cooled, and diluted to 150 c.c. A double precipitation with ammonia is not necessary, as the amount of iron to be separated is very small and does not carry down appreciable amounts of copper. The iron present at this stage, as also most of the copper, is derived chiefly from shots of matte which have been included in the slag. The standard colorimetric bottles are generally made up about once a month; they do not alter appreciably in colour over a much longer period, but the ammonia attacks the glass, forming a flocculent precipitate which, if shaken up in moving the bottles about, clouds the solution. The standards are, however, quickly renewed as follows: 0.5 g. of copper is dissolved in a little nitric acid, the red fumes boiled off, and the solution diluted to 500 c.c. Ten colorimetric bottles are taken, labelled 0.1, 0.2, 0.3, etc., 5 c.c. of nitric acid placed in each, then diluted, and from a burette, 1 c.c. of the above solution added to the first, 2 c.c. to the second, and an additional 1 c.c. to each successive bottle. Twenty c.c. of ammonia are then added to the contents of each bottle, after which they are filled with water up to the bottom of the labels, which are placed so that each solution has a volume of 150 c.c. For the colorimetric comparison, the bottles are placed on a level with the eye, on a narrow shelf covered and backed with white paper or tiles; there should be only one source of light, which should be directly behind the observer, and there should

<sup>1</sup> *Trans. Inst. Min. and Met.*, 1908-9, 18, 37.

be space enough on the shelf between the standard bottles to allow for the introduction of the bottle to be compared, which is moved along until its place in the series is determined. Since 2 g. of slag are taken, the factor on the corresponding bottle, divided by two, gives the percentage of copper in the slag.

## D. SPECIAL METHODS OF ANALYSIS

### I. COPPER ORES, MATTES, SPEISSES, AND SLAGS

#### 1. Determination of Copper.

The solution of the very finely powdered substance is effected, in general, as described on p. 158. Bituminous ores, such as "Kupferschiefer," are subjected to a preliminary roasting; very arsenical and antimonial ores and speisses are roasted carefully at a gradually increasing temperature. Treatment with nitric acid, aqua regia, or hydrochloric acid and potassium chlorate, is preferably followed by evaporation with an excess of sulphuric acid, so as to precipitate all the lead and a good deal of the antimony. In Nissenson and Neumann's method (p. 170), the small quantity of arsenic and antimony thrown down on precipitating the copper with a slight excess of sodium thio-sulphate, is completely removed by roasting. The sulphate solution, filtered from lead sulphate, is in many cases suitable for the direct gravimetric determination of the copper by electrolysis, and also for titration by one or other of the methods described.

*Copper Pyrites*, which is the most frequently occurring ore of copper, is assayed electrolytically, the solution used being considerably diluted on account of the large proportion of iron present. The volumetric methods of Low (p. 175) or Parkes (p. 173) can also be employed.

The copper in pyrites and in burnt pyrites may be estimated by Nahnsen's method<sup>1</sup> (*cf.* Vol. I., p. 286).

*Slags rich in Iron* are decomposed by hydrochloric acid, the residue containing the copper filtered off, ignited, and dissolved in nitric acid, and the copper estimated colorimetrically (p. 180).

*Refractory Slags* are treated with potassium fluoride and sulphuric acid in a platinum dish, as described on p. 181.

*Copper Speisses, Fahl Ores, Bournonite* ( $\text{CuPbSbS}_3$ ), etc., are best dissolved, according to Hampe,<sup>2</sup> by warming with a mixture of nitric and tartaric acids (for 1 g. of material 30 c.c. of nitric acid of sp. gr. 1.2 and 10 g. of tartaric acid), the diluted solution treated for a considerable time at 60° with sulphuretted hydrogen, and the precipitate extracted with hot potassium sulphide solution; the residue is then heated in a porcelain dish with nitric acid, evaporated with excess of sulphuric acid,

<sup>1</sup> *Chem. Zeit.*, 1887, **11**, 692.

<sup>2</sup> *Ibid.*, 1891, **15**, 443.



and the copper in the filtered solution either estimated electrolytically or determined by one of the volumetric methods.

T. Ulke<sup>1</sup> has given a description of the methods in vogue in the United States for the analysis of furnace products, slags, and plating baths.

## 2. Determination of Sulphur.<sup>2</sup>

Three-tenths of a gram of finely powdered copper pyrites, or of ores and mattes free from lead, is treated in an Erlenmeyer flask, standing in cold water, with fuming nitric acid, added in small quantities of 10 to 15 c.c. at a time, the action being allowed to go on for about an hour. The whole is then heated gradually in a water-bath, so that at the end of three hours it has reached a temperature of 70°, and in the course of another hour it is brought up to boiling point. Should particles of free sulphur be still present, the flask is cooled and the treatment with fuming nitric acid repeated. The solution is then evaporated to dryness in a porcelain dish, first without hydrochloric acid and then twice successively with 10 c.c. of pure hydrochloric acid, the residue taken up with dilute hydrochloric acid, filtered, and the boiling dilute solution precipitated with a slight excess of a boiling solution of barium chloride.  $\text{BaSO}_4 \times 0.1374 = \text{S}$ .

Speisses, fahl ores, raw and roasted copper matte and lead matte are, according to Hampe, examined as follows:—One gram of material is mixed with 6 g. of nitre and 5 g. of pure anhydrous sodium carbonate in a platinum crucible, the mixture covered with a little nitre and carefully fused. The melt is extracted with water, the lead precipitated by means of carbon dioxide and filtered off, and the filtrate, after being acidified with hydrochloric acid, evaporated to dryness; the residue is taken up with dilute hydrochloric acid, any silica filtered off, and the sulphur then precipitated in the ordinary way with barium chloride.

The following method gives good results with ores, mattes, and slags (Bannister):—Half a gram of the sample is treated with 10 c.c. of nitric acid, and when the first violent action ceases, crystals of potassium chlorate are added until the whole is decomposed. If globules of sulphur separate out, a few crystals or a little powdered potassium chlorate thrown on the top of the globules will cause them to go into solution at once. When all action has ceased, the solution is evaporated to dryness, 10 c.c. of hydrochloric acid added, and the whole evaporated to dryness to render the silica insoluble. The residue is then taken up with hydrochloric acid, the solution diluted with hot water, filtered, the filtrate made alkaline with ammonia, about 3 g. of barium chloride added, boiled for a few minutes, then acidulated with

<sup>1</sup> *Eng. and Min. J.*, 1889, 68, 728; *J. Soc. Chem. Ind.*, 1900, 19, 170.

<sup>2</sup> Cf. also, Vol. I., pp. 272 *et seq.*, and p. 289.



hydrochloric acid to redissolve the iron, again boiled for a few minutes, and allowed to settle well before filtering. Barium sulphate can in this way be separated in one operation from solutions containing large quantities of iron without contamination with the latter metal, as the iron is thrown out of solution before the precipitation takes place.

### 3. Determination of Silica.

The insoluble matter filtered off after decomposition of the ore or slag as described in the estimation of sulphur (p. 184), is ignited and weighed as "insoluble matter." In most cases for smelter routine work this is the only silica determination required, but in some cases it is necessary to determine the true silica content, when the following method may be used:—The insoluble residue is mixed in a platinum crucible with about 2 g. of sodium carbonate and fused over a blowpipe until all action ceases. The subsequent solution may be greatly facilitated by the following procedure:—The contents of the crucible are poured on to its lid, the crucible and lid each being held by a pair of platinum-tipped tongs; both crucible and lid are then placed in a porcelain dish containing about 40 c.c. of cold water. The bulk of the melt which is on the lid readily slides off, while the crucible only retains a thin film which is quickly dissolved out. The dish is heated until all is dissolved or thoroughly disintegrated, when the crucible is removed, the solution acidified with an excess of hydrochloric acid, evaporated to dryness, the residue, after cooling, moistened with 5 c.c. of hydrochloric acid and a few drops of nitric acid, diluted with hot water, filtered, washed, ignited, and weighed.

### 4. Determination of Alumina.

For the purposes of the copper smelter, the difference between the "insoluble matter" and "true silica" may generally be taken as alumina.

For the estimation of the alumina, 15 c.c. of a saturated solution of microcosmic salt are added to the filtrate from the silica, the volume of which should be about 100 c.c., which is then carefully neutralised with ammonia until a slight permanent white precipitate is obtained. This is heated to boiling and acidified with hydrochloric acid until the solution has cleared, care being taken not to have more than 2 c.c. of acid in excess; 25 c.c. of a saturated solution of sodium thiosulphate are then added and 5 c.c. of glacial acetic acid or an equivalent amount of dilute acetic acid. The solution is boiled for ten minutes, when a white precipitate, consisting of aluminium phosphate and sulphur, is obtained, which is easily filtered and washed. The precipitate is ignited very gently at first until the paper and sulphur are burnt off, and is then heated to a bright red

heat; it is quite white and should show no signs of fusion. The weight of  $\text{AlPO}_4$ , multiplied by 0.4184, gives the weight of  $\text{Al}_2\text{O}_3$ .

### 5. Determination of Iron and Lime.

In the case of ores, the filtrate from the separation of the insoluble matter is treated as follows:—The iron is precipitated with ammonia in the usual way and filtered, the precipitate dissolved in hydrochloric acid, reduced with stannous chloride, 20 c.c. of a saturated solution of mercuric chloride added, and the solution titrated with standard potassium bichromate in the usual way.

To determine the lime, an excess of ammonium oxalate is added to the filtrate from the iron, the solution boiled for a few minutes, filtered, and the filter paper and precipitate placed in a beaker containing 10 c.c. of sulphuric acid, diluted to 100 c.c., heated to boiling, and titrated with standard potassium permanganate solution in the usual way.

In the case of slags which can be dissolved in hydrochloric acid, the iron may be determined directly in the solution after reduction, by means of potassium bichromate.

For the determination of lime in slags, the filtrate from the silica is heated to nearly boiling, a decided excess of ammonia added, then solid oxalic acid until the ferric hydroxide has all dissolved; ammonia is again added until there is a slight permanent precipitate of ferric hydroxide, the solution again cleared by the careful addition of small quantities of oxalic acid, boiled and filtered. The precipitate is treated as above with sulphuric acid and titrated with standard permanganate, containing 5.635 g. per litre; 1 c.c. = 0.005 g.  $\text{CaO}$ .

## 2. MARKETABLE COPPER (TOUGH COPPER AND ELECTROLYTIC COPPER)<sup>1</sup>

The commercial analysis of marketable copper is frequently necessary, as even comparatively small amounts of impurities have a considerable effect on the properties of the metal and of its alloys.

The investigations of Hampe<sup>2</sup> have shown that the properties of refined copper depend largely on the form of combination of the metallic or other impurities, according as to whether they are alloyed with the copper or dissolved as oxidised compounds.

The analytical methods for the investigation of copper and for the determination of these forms of combination, as introduced by Hampe himself and, in continuation of his work, by Stahl,<sup>3</sup> are of scientific

<sup>1</sup> Cf. Fresenius, *Quantitative Analysis*, 7th edition, vol. ii., p. 400; A. Hollard, *Chem. Zeit. Rep.*, 1900, 24, 146.

<sup>2</sup> *Zeit. f. d. Berg., Hütten u. Salinenwesen in dem preuss. Staate*, 21, 218; 22, 93; *J. Chem. Soc.*, 1876, 29, 973; *Z. anal. Chem.*, 1874, 13, 179.

<sup>3</sup> *Ueber Raffination, Analyse und Eigenschaften d. Kupfers*, by W. Stahl, Clausthal, 1886.

interest and also of considerable practical importance in connection with the refining of copper. As the quantitative determination alone of the foreign constituents of marketable copper, without reference to their mode of combination, occupies several days, and is quite sufficient if the copper is required for the manufacture of alloys, the commercial investigation is confined either to the complete quantitative analysis, or sometimes to the determination of the copper and of the more detrimental impurities, such as bismuth, antimony, and arsenic only.

The quality of the metal cannot be gauged from the fracture; a sample of Japanese copper, of "Furnkawa" brand, for instance, examined by Pufahl, contained 0.78 per cent. of arsenic, yet it showed an excellent fracture. Such tests as hammering, bending, tenacity, etc., will show the value of the metal as such, but they give no information as to whether the copper can be used for the production of alloys of the best quality.

Some alloys can only be produced with very pure copper, *e.g.*, for making thin sheet brass, copper is required which is free from bismuth and antimony, and contains not more than 0.1 per cent. of arsenic; phosphor bronze of high tenacity must be made from the purest copper and tin, and so on.

Electrolytic copper, which is now manufactured in considerable quantities, is almost chemically pure; it contains usually only traces of sulphur, in the form of interlocked sulphate solution, and frequently also recognisable amounts of bismuth, antimony, arsenic, iron, selenium, and tellurium.

Refined copper usually contains 0.05 to 0.2 per cent. of oxygen (as cuprous oxide and oxidised compounds of antimony, arsenic, lead, bismuth, nickel, etc.); the impurities proper, *viz.*, arsenic, antimony, tin, lead, nickel, cobalt, iron, sulphur, selenium, and tellurium, in the better classes of copper, do not amount to over 0.7 per cent.

Silver is seldom present to a greater extent than 0.03 per cent., and gold occasionally in traces. The best brands of copper are the Lake Superior, South Australian Wallaroo and Burra-Burra, English "Best Selected," and Mansfeld refined.

### 1. Complete Analysis.

After the introduction of electrolytic methods for the estimation of copper, Hampe, in 1873 (*loc. cit.*), recommended the electrolytic deposition of copper from a solution of 25 to 30 g. of marketable copper, and the determination of the impurities in the solution, from which the whole or most of the copper had been removed; as bismuth is deposited with the copper, the deposited metal must be redissolved, the nitrate solution boiled down with hydrochloric acid, and the bismuth precipitated as oxychloride.



This method was, however, discarded by many, since Hampe subsequently ascertained<sup>1</sup> that, in addition to bismuth, small amounts of arsenic and antimony may come down with the copper. He determined the antimony deposited with the copper, by dissolving the electrolytic deposit and precipitating the copper in the solution as thiocyanate; this method is fully described later on (p. 192).

On R. Finkener's recommendation, P. Jungfer<sup>2</sup> investigated the method introduced by Flajolot,<sup>3</sup> in which copper is separated from arsenic and antimony by precipitation as cuprous iodide, and, as an outcome of his work, he introduced the following accurate and rapid method of copper analysis:—

**(a) Jungfer's Iodide Method.**—Most of the copper is precipitated from a slightly acid nitrate or sulphate solution as cuprous iodide, by addition of potassium iodide in presence of sulphuric acid, sulphur dioxide, and a little potassium fluoride, which forms easily soluble antimony-potassium fluoride; the free sulphur dioxide is removed from the filtrate, the copper remaining in solution, together with the arsenic and antimony, and any bismuth and lead, is precipitated with sulphuretted hydrogen, and the copper, bismuth, and lead separated from a strong ammoniacal solution of the sulphides, after addition of tartaric acid, according to R. Finkener's method,<sup>4</sup> by carefully adding small quantities of weak sulphuretted hydrogen water and warming. Nickel, cobalt, manganese, and iron may be estimated in the filtrate from the sulphides. Bismuth comes down principally with the cuprous iodide, and is, therefore, determined in a separate portion by Jungfer's method (p. 192); silver is also determined in a separate portion.

If the copper under examination dissolves in nitric acid without residue, and only arsenic and antimony are to be estimated, precipitation may be effected directly in the nitrate solution; otherwise, it is necessary to evaporate with sulphuric acid to precipitate the lead, and so on.

To carry out the determination, 10 g. of the copper, in the form of clean chippings or drillings, are dissolved in a large covered porcelain dish, in 40 c.c. of pure nitric acid of sp. gr. 1.4, added a little at a time, 10 c.c. of redistilled sulphuric acid, diluted with 10 c.c. of water, added, and the whole evaporated to dryness on a water-bath, and then heated on a sand-bath until sulphuric vapours begin to come off. The cooled mass is dissolved by warming with 150 c.c. of water, and, after standing for several hours in the cold, the lead sulphate, together with any

<sup>1</sup> *Chem. Zeit.*, 1892, **16**, 417; *J. Soc. Chem. Ind.*, 1892, **11**, 695.

<sup>2</sup> *Berg. u. Hütten. Zeit.*, 1887, **46**, 490; *Z. anal. Chem.*, 1888, **27**, 63; *J. Chem. Soc. Abstr.*, 1888, **54**, 324.

<sup>3</sup> *Annales des Mines*, 1853, p. 641; *J. prakt. Chem.*, 1854, **61**, 105.

<sup>4</sup> *Mitteil. der Kgl. techn. Versuchsanstalten zu Berlin*, 1889, p. 76; *J. Soc. Chem. Ind.*, 1889, **8**, 733.



antimonic acid and lead antimoniate, is filtered off on a small filter. The further treatment of the impure lead sulphate is carried out as described below.

The filtrate is transferred to a large beaker, diluted to about 300 c.c., 150 mg. of potassium fluoride, free from arsenic, added, then 50 c.c. of a pure aqueous solution of sulphur dioxide, followed by the calculated amount of potassium iodide, dissolved in a little water and added little by little with stirring. Any iodine set free is removed by means of an aqueous solution of sulphur dioxide.

Ten grams of pure copper require 26.2 g. of pure potassium iodide. The copper may be taken as 99 per cent. pure, so that only 26 g. of potassium iodide are added, the cuprous iodide being appreciably soluble in excess of potassium iodide solution.

When the final portions of potassium iodide and sulphurous acid have been added, the mixture is warmed on a boiling water-bath; the dense greyish white precipitate settles in about ten minutes. The supernatant liquid, which is usually colourless, though occasionally of a faint greenish yellow colour, is decanted as completely as possible through a filter paper, the precipitate washed three or four times by decantation with 100 c.c. of hot water containing a little sulphuric acid, the free sulphur dioxide in the combined filtrates oxidised by iodine solution, and then sulphuretted hydrogen passed for a considerable length of time through the warmed liquid.

The sulphide precipitate, which contains all the arsenic and antimony, the copper not previously precipitated, and any bismuth, is collected on a filter, washed with water containing a little sulphuric acid and sulphuretted hydrogen, and dissolved off the filter with hydrochloric acid and a little potassium chlorate; the solution, after the addition of a few decigrams of tartaric acid and after dilution to 50 c.c., is rendered strongly alkaline with ammonia. Copper (and bismuth) are then separated out as sulphides, by Finkener's method, adding small quantities of dilute sulphuretted hydrogen water and warming gently; the precipitate is quickly filtered off and washed with water containing a drop of ammonium sulphide; the filtrate from this precipitate is acidified with dilute sulphuric acid and warmed, and the arsenic and antimony precipitated with sulphuretted hydrogen.

The impure lead sulphate mentioned above is, after drying, removed as far as possible from the filter paper, which is itself destroyed by being treated with concentrated nitric acid in a porcelain crucible, the acid being evaporated off and the residue carefully heated with a little ammonium nitrate; the main bulk of the lead sulphate is mixed with from three to six times its weight of a mixture of equal parts of sulphur and sodium carbonate, placed in a crucible, the cover put on, and the mixture fused at a moderate temperature. The melt is extracted with

hot water and the lead sulphide (containing some bismuth and copper) filtered off and washed, first with a dilute potassium sulphide solution, and then with dilute sulphuretted hydrogen water. The impure lead sulphide is converted into sulphate by treatment with nitric acid and evaporation with sulphuric acid, and weighed (*cf.* Lead, p. 222). From the sulphuric acid filtrate any small quantity of bismuth may be precipitated by neutralising with ammonia, adding a little ammonium carbonate, and warming for some time; the separated basic carbonate is dissolved in a little hydrochloric acid, most of the free acid removed by evaporation and the bismuth precipitated, as oxychloride, by diluting largely with water. The estimation of bismuth in the impure lead sulphate is necessary, if the bismuth estimation in the copper is to be carried out by the Jungfer method.

Antimony and sulphur are precipitated from the sulpho-salt solution by adding excess of dilute sulphuric acid and warming; the washed precipitate is treated on the filter paper with hydrochloric acid and a little potassium chlorate.

The mixture of antimony and arsenic sulphides, obtained from the filtrate from the cuprous iodide, is treated similarly. To the combined solutions a little tartaric acid is added, then a good excess of ammonia, magnesia mixture (made from magnesium chloride), and one-third the volume of absolute alcohol; the whole is allowed to stand, covered, for forty-eight hours, to enable the magnesium ammonium arsenate to precipitate completely. The precipitate is then filtered off, washed with a mixture of one volume of strong ammonia, three volumes of water, and two volumes of absolute alcohol, and weighed as magnesium pyroarsenate.

The filtrate is gently heated to drive off the alcohol and most of the ammonia, acidified with sulphuric acid, and the antimony precipitated with sulphuretted hydrogen. The precipitate is filtered off and washed with weak sulphuretted hydrogen water. If the precipitate contains apparently only a few milligrams of antimony, it is dissolved on the filter with yellow ammonium sulphide, the solution evaporated to dryness in a porcelain crucible, then oxidised with nitric acid and the antimony weighed as antimony tetroxide,  $\text{Sb}_2\text{O}_4$  (*cf.* Antimony). In the case of larger quantities of antimony sulphide, the precipitate is washed off the filter paper into a porcelain dish, evaporated to dryness on the water-bath, after which the dish is covered and fuming nitric acid run in from a pipette; the antimony sulphide is oxidised to the oxide and to sulphuric acid, with practically no separation of sulphur. Meanwhile any antimony sulphide remaining on the filter paper is dissolved in a little ammonium sulphide and the solution evaporated to dryness in a porcelain crucible on the water-bath. The contents of the dish are transferred to this crucible, oxidised with nitric acid, evaporated, the

sulphuric acid driven off, and the residue ignited in the open crucible, finally for a couple of minutes over the blowpipe, and weighed as antimony tetroxide.

Nickel, cobalt, iron, and also manganese are precipitated together in the filtrate from the sulphide precipitate. The solution is heated to boiling in a large porcelain dish, the sulphuretted hydrogen oxidised with bromine water, and the precipitation then effected with pure sodium or potassium hydroxide, the precipitate filtered off and washed with boiling water; the mixture of hydroxides is then dissolved in hot, dilute sulphuric acid, with addition of a little aqueous sulphurous acid, the solution evaporated on the water-bath, and finally taken to dryness with a few drops of nitric acid. The residue, which should not smell of acid, is taken up with water, the solution cooled, neutralised with sodium carbonate, a little sodium acetate added (about six times the amount of the presumed iron), and the whole heated to boiling; after five minutes the basic acetate of iron is filtered off, redissolved in a little hydrochloric acid, the solution diluted with water, warmed, nearly neutralised with sodium carbonate, potassium iodide added, and the solution titrated with sodium thiosulphate.<sup>1</sup> Five cubic centimetres of carbon bisulphide should be added, shaken up, and allowed to stand for half an hour before titration with the thiosulphate. The filtrate is concentrated by evaporation, transferred to a weighed platinum crucible of 100 to 150 c.c. capacity, ammonium sulphate and excess of ammonia added, and the nickel and cobalt deposited together electrolytically in the platinum crucible (*cf.* Nickel, p. 308). Any manganese present separates as a brownish black flocculent precipitate of hydrated peroxide, a portion of which deposits on the anode but which can be easily removed. The hydrated manganese peroxide is collected on a small filter paper, washed with hot water, the filter with precipitate incinerated in a crucible, ignited strongly in presence of air, and weighed as  $Mn_3O_4$ .

If the copper under investigation contains tin, this is separated as metastannic acid, together with antimonious acid and lead antimoniate, by boiling the diluted nitrate solution; the filtered solution is cooled and treated with potassium iodide, and so on. The dried precipitate is then fused with sodium carbonate and sulphur, the arsenic, antimony, and tin precipitated as sulphides, and dissolved in hydrochloric acid and a little potassium chlorate; this solution is heated gently for some time to remove free chlorine, cooled, treated with a considerable quantity of pure hydrochloric acid of sp. gr. 1.19, and the arsenic precipitated alone, as sulphide, by passing sulphuretted hydrogen for a considerable time (R. Finkener's method). The liquid, after standing for several hours under a bell-jar, must still smell of sulphuretted hydrogen, otherwise

<sup>1</sup> *Cf.* Pszczolka, *Chem. News*, 1885, 47, 107; Parthiel, *J. Iron and Steel Inst.*, 1890, 1, 374; Carnegie, *Chem. News*, 1891, 60, 87.



more gas must be passed in ; the precipitate is filtered off through an asbestos filter and washed, first with strong hydrochloric acid saturated with sulphuretted hydrogen, and finally with pure water. It is then dissolved off the filter with warm ammonia, the solution evaporated in a porcelain dish, and the residue oxidised with fuming nitric acid in a covered dish and evaporated to dryness ; the arsenic is then precipitated as ammonium magnesium arsenate.

The hydrochloric acid filtrate from the arsenic sulphide is diluted largely with water, a portion of the free acid neutralised with ammonia, and the tin and antimony precipitated as sulphides by a current of sulphuretted hydrogen; the precipitated sulphides are dissolved in hydrochloric acid and treated with iron, which precipitates the antimony quantitatively, whilst the tin remains in solution as stannous chloride. The tin is precipitated in the filtrate from the antimony as dark brown stannous sulphide by means of sulphuretted hydrogen (*cf.* Tin, p. 260).

The noble metals in marketable copper and in blister copper (black copper) are determined by scorifying with lead, concentrating and cupelling (*cf.* Silver, p. 110), or they may be determined by the Combined Wet and Dry Method described on p. 109.

The estimation of bismuth by Jungfer's method (*loc. cit.*) is carried out as follows:—Ten grams of copper are dissolved in about 50 c.c. of nitric acid (sp. gr. 1.4), the clear solution diluted with 100 c.c. of cold water, and dilute sodium hydroxide solution added, with stirring, until a slight permanent precipitate is produced ; the liquid is then stirred for a few minutes and allowed to stand for one or two hours. The whole of the bismuth which is precipitated after allowing to settle well is filtered off, washed thoroughly, dissolved in a little hydrochloric acid, most of the free acid evaporated off, and the bismuth precipitated as oxychloride, by dilution with about a litre of water ; after standing for from two to three days, the oxychloride is collected on a small filter paper, dried at 110°, and weighed.

The amount of pure potassium iodide used in this method is considerable ; the cuprous iodide is kept, washed by decantation with water, then stirred to a thin paste, and heated with an excess of clean iron turnings ; the colourless solution of ferrous iodide is filtered off and the iron precipitated with a sufficiency of pure potassium carbonate, after which the solution of potassium iodide may be evaporated and the potassium iodide crystallised out.

**(b) Hampe's Thiocyanate Method.**<sup>1</sup>—A sulphate solution of the sample is made and filtered from lead sulphate and insoluble cuprous and bismuth antimonates, the filtrate collected in a 2 litre flask, sulphur dioxide passed in, and the copper almost completely precipitated in the cold by means of a carefully measured amount of an aqueous

<sup>1</sup> *Chem. Zeit.*, 1893, 17, 1691 ; *J. Soc. Chem. Ind.*, 1894, 13, 421.



solution of pure potassium thiocyanate; a little copper, and the whole of the arsenic, antimony, tin, bismuth, nickel, cobalt, iron, and manganese remain in solution and are estimated by the methods described above (Method (a)).

To carry out the determination, 25 g. of copper are dissolved by warming in a large beaker with a mixture of 200 c.c. of water, 100 c.c. of pure sulphuric acid, and 45 to 46 c.c. of nitric acid (sp. gr. 1.21). According to the equation—



the amount of nitric acid used is sufficient for the oxidation of the copper, and very little excess remains in the solution. After diluting with 200 c.c. of water, the lead sulphate is filtered off and treated as described above (Method (a)). To decompose the nitric acid, sulphur dioxide is passed into the filtrate, warmed to about 40°, so long as red fumes are evolved. Further treatment with sulphur dioxide precipitates metallic silver, and the addition of a few drops of hydrochloric acid precipitates the remainder of the silver as chloride; after standing for twenty-four hours, the silver precipitate is collected on an ash-free filter paper, the paper incinerated, and the silver chloride reduced by hydrogen to metallic silver, or it may be scorified with a little lead and then cupelled.

The solution is then transferred to a 2 litre flask, a rapid current of sulphur dioxide passed in, and the amount of potassium thiocyanate, nearly sufficient for the precipitation of the copper added, little by little, in aqueous solution; the strength of the potassium thiocyanate solution must have been previously ascertained by standardising with silver solution (*cf.* Silver, p. 117); 107.88 parts of silver are equivalent to 63.57 parts of copper. About 500 c.c. of the thiocyanate solution should be sufficient for the precipitation of 25 g. of copper. The treatment with sulphur dioxide is discontinued as soon as the liquid, after shaking, smells distinctly of the gas. The delivery tube is then removed, and the flask filled to the mark with water; the liquid cannot be mixed in the flask, on account of the dissolved sulphur dioxide, but must be poured into a large dry beaker and then well mixed by stirring.

When the thiocyanate has settled fairly completely, the greater part of the solution is filtered through a dry pleated filter paper into a large dry beaker, and a measured portion, say exactly 1800 c.c., taken for analysis (*cf.* Method (a), p. 188).

The sulphur dioxide is driven off by heating the liquid, and sulphuretted hydrogen then passed for some time. The filtrate from the sulphide precipitate contains a good deal of free sulphuric acid, owing to a considerable excess having been used for the solution of the copper in order to prevent the precipitation of basic salts of bismuth

and of antimony during the dilution to 2 litres; before precipitating the nickel, cobalt, iron, and manganese with ammonia and ammonium sulphide, or with sodium hydroxide, the greater portion of this free sulphuric acid should be removed by evaporating down and heating the concentrated solution on a sand-bath. The above metals are then precipitated from the solution, after again diluting, and their separation effected by the usual methods (*cf.* Method (a)). In the analysis of particularly pure brands of copper, 25 c.c. of sulphuric acid will suffice for 25 g. of copper.

For the calculation of the results, the volume occupied by the thiocyanate precipitate produced by 25 g. of copper must be known; according to Hampe, its specific gravity is 2.999. The amount obtained from 25 g. of copper thus occupies 15.983 c.c.; hence, the supernatant liquid in the 2 litre flask occupies  $2000 - 15.983 = 1984.017$  c.c. Assuming that from 1800 c.c. of filtrate the arsenic obtained was 0.102 g., the amount in the whole 25 g. of copper would be

$$= \frac{0.102 \times 1984.017}{1800} \text{ g.}$$

Hampe tested this method very carefully and obtained excellent results.

Copper, oxygen, sulphur, and phosphorus are determined in separate samples. Selenium and tellurium separate with the silver, on passing in sulphur dioxide; they are determined as described on p. 202.

For the determination of the noble metals, *cf.* the sections on Silver and Gold.

## 2. Separate Estimations.

The separate estimation of the several constituents in marketable copper is much more frequently required than the lengthy complete analysis.

**Copper.**—Five grams of an average sample are dissolved in 20 c.c. of nitric acid of sp. gr. 1.4, and the solution diluted to 250 c.c.; 50 c.c., corresponding to 1 g. of material, are then taken for the electrolytic deposition of the copper (pp. 159 *et seq.*). This method is extensively used for blister-copper and for marketable copper, in copper refineries. Impure copper, containing arsenic, antimony, and bismuth, is dissolved off the cathode, one portion examined for bismuth and a second portion precipitated with sulphuretted hydrogen and the copper sulphide separated from the impurities according to the sulphide method described on p. 169.

**Total Oxygen.**—Ten grams of clean drillings are heated in a hard glass bulb, in a current of pure dry hydrogen, at a dull red heat for about an hour; the time, however, varies according to the size of the drillings;<sup>1</sup> for strips, two hours, for  $\frac{1}{4}$ -inch cubes, five hours, are

<sup>1</sup> Archbutt, *Analyst*, 1905, 30, 385.

necessary, etc. The narrow end of the bulb-tube should be drawn out to a length of about 20 cm. In the case of samples containing much arsenic and antimony, these constituents volatilise partially and form a mirror-like deposit in the narrow tube. Small quantities of sulphur (probably due to sulphur dioxide, absorbed by the copper) may be evolved in the form of sulphuretted hydrogen, which may be oxidised in a small bulb by means of a mixture of hydrochloric acid and bromine and subsequently estimated as barium sulphate.

After allowing to cool and displacing the hydrogen by air, the loss of weight is ascertained; this loss, less the sulphur, is equal to the total oxygen. Refined copper contains from 0.05 to 0.2 per cent. of oxygen. Traces of oxygen have been found in electrolytic copper; its presence is due, in all probability, to enclosed copper liquor.

If the copper contains very little arsenic and antimony, which has been previously estimated, the heating in hydrogen may be carried out in a porcelain boat, placed in a combustion tube.

The hydrogen is produced in a Kipp generator, from pure zinc and pure dilute sulphuric acid, and is purified and dried by passing through small wash-bottles, containing an alkaline lead solution, silver nitrate solution, and distilled sulphuric acid respectively, and the drying completed by passing the gas through a U-tube containing pumice soaked in sulphuric acid.

The estimation of the oxygen, present as cuprous oxide, which enables an estimate of the forms of combination of the impurities to be arrived at, is fully described in the original paper by Hampe (*loc. cit.*).<sup>1</sup>

**Sulphur.**—The best method for this estimation is that proposed by Lobry de Bruyn.<sup>2</sup> Five grams (less in the case of blister-copper) are dissolved in pure nitric acid, the solution diluted, and the copper deposited electrolytically. To remove nitric acid, the solution is heated first over the free flame and finally on a water-bath; the residue, which consists chiefly of ammonium nitrate, is evaporated twice with 50 c.c. of pure hydrochloric acid, then taken up with hydrochloric acid and water, and the boiling solution precipitated with barium chloride solution.

**Phosphorus.**—This element is seldom found in marketable copper, and then only in traces. If the copper be free from arsenic, a concentrated solution, containing but little free nitric acid, may be treated directly in the cold with molybdate solution and a considerable quantity of solid ammonium nitrate; the precipitate of ammonium phospho-molybdate is filtered off after standing for twenty-four hours, and the precipitate treated as described later under phosphor-copper (p. 205).

<sup>1</sup> Cf. also, Fresenius, *Quantitative Analysis*, 7th ed., vol. ii., p. 404.

<sup>2</sup> *Rec. Trav. Chim.*, 10, 125; *Chem. Zeit. Rep.*, 1891, 15, 354; *J. Chem. Soc. Abstr.*, 1892, 62, 753.



In the case of copper containing arsenic, which is present in most brands, 10 g. are dissolved in just sufficient nitric acid, the solution diluted to 200 c.c. and treated with sodium carbonate, as in the estimation of bismuth by Jungfer's method (p. 192); sufficient sodium carbonate is added to the neutralised solution to precipitate about 0.2 g. of copper. The hydrochloric acid solution of the filtered precipitate is treated in a flask with 20 c.c. of aqueous sulphurous acid, then boiled until it no longer smells of sulphur dioxide, and diluted; sulphuretted hydrogen is then passed into the warm solution, which precipitates copper, bismuth, lead, and arsenic as sulphides. The filtrate from this precipitate is evaporated, the residue again evaporated with 5 c.c. of nitric acid, taken up with a few drops of nitric acid and a little water, and treated with molybdate solution in the usual way. The phosphoric and arsenic acids are completely precipitated with the copper carbonate; it is best, however, to warm the turbid liquid for several hours in a water-bath with frequent stirring, instead of simply stirring, as recommended by Jungfer.

**Arsenic.**—This is rapidly determined by E. Fischer's distillation method.<sup>1</sup> The arsenic from 10 g. of copper is first precipitated as basic arsenate, together with copper carbonate, as described above, the precipitate filtered off, dissolved on the filter in a little concentrated hydrochloric acid, and the filter paper washed with concentrated hydrochloric acid; to this solution, contained in a flask of about 300 c.c. capacity, 10 g. of ferrous sulphate and 75 c.c. of pure fuming hydrochloric acid are added. (Instead of the ferrous sulphate, 10 g. of Mohr's salt, or, according to Clark, 5 g. of solid cuprous chloride,<sup>2</sup> may be used.) A white rubber stopper, provided with a 3-mm.-wide tube, bent at an angle of 70° and having each limb 10 cm. in length, is fixed into the neck of the flask; the tube is connected, by means of a piece of strong rubber tubing, with a 50 c.c. pipette, the end of which dips several millimetres below the surface of air-free water, contained in a beaker.

The flask is placed on an asbestos tray, the contents heated to boiling, and the heating continued until about half the liquid has distilled over; the whole of the arsenic is thus volatilised as arsenious chloride.<sup>3</sup> The arsenic in the liquid is determined gravimetrically by gently warming, and then precipitating the arsenic as sulphide by means of sulphuretted hydrogen, filtering through a tared filter, drying for three hours at 105° to 110°, and weighing the pure sulphide.  $\text{As}_2\text{S}_3 \times 0.6093 = \text{As}$ .

F. Mohr's volumetric method is equally accurate. The distillate is neutralised with sodium carbonate, 20 c.c. of a cold saturated solution

<sup>1</sup> *Ber.*, 1880, **13**, 778; *cf.* also, Piloty and Stock, *Ber.*, 1897, **30**, 1649; Beck and Fisher, *Chem. News*, 1899, **80**, 259.

<sup>2</sup> *Cf.* Vol. I., p. 285.

<sup>3</sup> *Cf.* also, the method described on p. 239.

of sodium bicarbonate are added, and a little freshly prepared starch solution, and the solution titrated with iodine solution (*cf.* Vol. I., p. 122):—



In Fischer's distillation method, as later investigations have shown, several distillations are necessary for the complete volatilisation of the arsenic, unless very strong solutions of hydrochloric acid, or the gas itself, are used in the operation. Odling<sup>1</sup> dissolves the copper in ferric chloride and hydrochloric acid, and continues to boil after complete solution has been effected, when the arsenic distils over as arsenious chloride; to raise the boiling point, and so ensure the complete volatilisation of the arsenic, T. Gibb<sup>2</sup> adds calcium chloride to the hydrochloric acid solution of ferric chloride. Beringer<sup>3</sup> found that on boiling a solution of ferric chloride and hydrochloric acid with copper containing 3.48 per cent. of arsenic, only 2.74 per cent. was volatilised by one evaporation; whereas, with the addition of calcium chloride, the whole of the arsenic was volatilised. Usually it is sufficient to work on 1 g. of copper; this should be completely dissolved in fifteen minutes. The arsenic in the distillate is determined by means of very dilute iodine solution. (*Cf.* also the following section on the Estimation of Antimony.)

**Antimony.**—The separate estimation of antimony is seldom carried out; it is usually estimated in conjunction with arsenic in the filtrate from cuprous iodide or thiocyanate (*cf.* Complete Analysis, sections (a) and (b)). Brands containing much antimony, which are useless for alloys except ordinary cast brass, seldom come on the market.

An excellent and rapid volumetric method for the estimation of antimony, and, at the same time of arsenic, in copper and cupreous materials generally, is due to Allan Gibb.<sup>4</sup> The ferric chloride and calcium chloride mixture, as used for the distillation of arsenic, solidifies at a temperature which is below that at which antimonious chloride is volatile, but, if the calcium chloride and ferric chloride be replaced by a saturated solution of zinc chloride, a temperature is readily attained at which antimonious chloride can be volatilised; the antimonious chloride is, however, not entirely carried over into the condensing apparatus, a portion of it collecting in the neck of the distillation flask, owing to insufficient flow of gas to carry it over. Practically the whole of the hydrochloric acid is driven off before the antimonious chloride begins to volatilise, and it is essential, therefore, to introduce at this stage some material which shall cause a flow of gas sufficient to carry over the antimonious chloride. The difficulty is surmounted by the

<sup>1</sup> *Chem. News*, 1863, 8, 27.

<sup>2</sup> *Ibid.*, 1882, 45, 218.

<sup>3</sup> *Text Book of Assaying*, 12th ed., 1910, p. 385.

<sup>4</sup> *J. Soc. Chem. Ind.*, 1901, 20, 185.

introduction of hydrochloric acid when the requisite temperature has been reached.

The interval in both time and temperature between the volatilisation of the arsenic and antimony allows of each of the chlorides being collected separately with absolute certainty.

To ensure the reduction of the arsenate and antimoniate, it is well to dissolve part, at least, of the copper in the distillation flask, and it is, therefore, necessary that a reagent capable of bringing the copper rapidly into solution should be added to the acid solution of zinc chloride. As suitable mixtures of zinc and ferric chlorides solidify at temperatures below that necessary for the distillation of antimonious chloride, ferric chloride is not available as a solvent; a mixture of zinc and cupric chlorides with hydrochloric acid serves well, however, and such a mixture remains liquid at a temperature considerably over 200°.

The process is carried out as follows:—The weighed sample is dissolved in nitric acid or aqua regia, and the solution, diluted to about 250 c.c., heated nearly to boiling; in the absence of an appreciable amount of iron in the sample, 1 c.c. of a saturated solution of ferric chloride is added, and then solid sodium bicarbonate, until a small permanent precipitate is produced in the hot solution. This precipitate carries down with it all the arsenic and antimony as basic ferric salts. The precipitate is allowed to settle, filtered off through a small filter paper, washed with hot water to remove nitrates, and introduced into the distillation flask with 50 c.c. of the mixture of zinc chloride, cupric chloride, and hydrochloric acid.

This solution is made by mixing a saturated solution of zinc chloride with an equal volume of hydrochloric acid containing 100 g. of copper per litre, in the form of cupric chloride; it should boil at about 108°, and is accordingly concentrated or diluted as required.

About 0.25 g. of pure electrotype copper must be introduced into the flask together with the precipitate to act as a reducing agent towards the arsenic and antimonious acids, though when the material under examination is metallic copper itself, a portion of the weighed sample may be reserved and used instead, as mentioned above.

The most suitable apparatus for the distillation is an ordinary round-bottomed 250 c.c. fractionating flask, in the neck of which is a rubber stopper provided with two holes, through which pass a thermometer reaching down to within half an inch from the bottom of the flask, and a small tap-funnel containing hydrochloric acid; the stem of this funnel reaches about half-way into the body of the flask, and is, after being drawn out to a point, bent so as to carry the cold hydrochloric acid away from the thermometer, and so obviate the danger of cracking the bulb. The end of the delivery tube from the flask is bent and passed through a stopper in one arm of a three-bulb U-tube, standing in cold water, in



which the distillate is condensed; the U-tube contains just sufficient water to form a lute. The flask is first heated over wire gauze by a flame which just suffices to produce gentle ebullition, until the thermometer registers  $115^{\circ}$ ; the whole of the arsenic has by this time come over and the condensing tube is removed and a fresh one attached. It is unnecessary to remove the burner and so cool the flask during this changing of condensers, as no antimony will come over. The wire gauze is then removed and the flask heated over a free flame until the temperature reaches  $150^{\circ}$  to  $160^{\circ}$ , which occurs in from ten to fifteen minutes; about 10 c.c. of hydrochloric acid are then run in cautiously from the tap-funnel. As the acid enters the flask, dense white fumes are evolved, and the flow is regulated so that a steady stream of gas passes from the flask; care must be taken that no liquid acid falls on the fused zinc chloride. The heating is continued until the flask is cleared of fumes, when the temperature is usually about  $200^{\circ}$ ; the second distillate is then removed, the fittings of the flask disconnected, and the contents allowed to cool, when the solidified chlorides may be removed with warm water.

The titration of the distillates is effected with iodine solution, made by dissolving 0.85 g. of iodine and 2 g. of potassium iodide in about 25 c.c. of water and making up to a litre; 1 c.c. of this solution is equivalent to 0.00025 g. of arsenic or to 0.0004 g. of antimony. The titration is carried out as follows:—The distillates are washed into separate flasks and a little tartaric acid added to the antimony distillate; the acid solutions are neutralised with ammonia, slightly acidified with hydrochloric acid, and about 2 g. of sodium bicarbonate added to each. Starch solution is used as indicator, and it is necessary that this should be coloured by iodine before addition to the assay, as a considerable quantity of iodine, frequently 0.2 to 0.3 c.c., is required to effect a coloration, when using the weak standard solution employed in determining the small amounts of arsenic and antimony usually found in cupreous materials.

**Bismuth.**—This metal is one of the most detrimental of the impurities in copper; as little as 0.05 per cent. of bismuth, present as metal, not as antimoniate or arsenate, produces cold-shortness in copper, and also in a high degree red-shortness. For this reason, some refiners refuse copper containing bismuth.

Jungfer's method of estimating bismuth has been described above, p. 192. The following is the method employed at the "Königliche chemisch-technische Versuchsanstalt" at Berlin:—Ten grams of copper are dissolved in a beaker in 60 c.c. of nitric acid (sp. gr. 1.3), any residue being filtered off and fused with sodium carbonate and sulphur, as described under the heading, "Complete Analysis," section (a); the clear solution is so far neutralised with pure sodium hydroxide, that a

Congo red test paper is rendered only faintly blue, and is then transferred to a 5 litre flask, diluted with 4 litres of distilled water, 5 g. of sodium chloride added, and the whole well shaken. (The sodium chloride keeps the small quantity of silver chloride in solution.) After standing for three days, the precipitate is completely settled, and the clear liquid may be syphoned off and filtered; the precipitate is washed on the filter paper, dissolved in a little hydrochloric acid, the solution made slightly alkaline with ammonia, and the bismuth-iron-antimony precipitate filtered off, washed, and dissolved in a little hot nitric acid of sp. gr. 1.2. Sulphuretted hydrogen is then passed into the diluted solution, and the resulting precipitate is treated on the filter with yellow ammonium sulphide; the bismuth sulphide, which remains behind, is dissolved in hot nitric acid (sp. gr. 1.2), the solution rendered slightly ammoniacal, and the washed bismuth hydroxide precipitate, which is now quite free from sulphuric acid, dissolved off the filter with hot nitric acid, and the solution evaporated in a large porcelain crucible; the residue is heated first on a hot-plate or sand-bath, then over a free flame, and finally gently ignited and weighed as bismuth oxide.  $\text{Bi}_2\text{O}_3 \times 0.8968 = \text{Bi}$ .

The method of Fernandez-Krug and Hampe<sup>1</sup> is based on that of Fresenius and Haidlen<sup>2</sup> for the separation of copper and bismuth by means of potassium cyanide solution. Ten grains of copper are dissolved in 40 c.c. of nitric acid (sp. gr. 1.4) and the solution evaporated to dryness in a platinum or porcelain dish, on a water-bath, with 20 c.c. of dilute sulphuric acid (1 to 1); the residue is heated on a hot-plate, until evolution of sulphuric fumes commences, the cooled mass dissolved by warming with 175 c.c. of a mixture of 25 c.c. of dilute sulphuric acid (1 to 1) and 150 c.c. of water, the solution cooled, and the lead sulphate, which is free from bismuth, filtered off.

Bismuth arsenate, which is insoluble in nitric acid, may be separated in the first instance. The lead sulphate, after being weighed, is examined for antimony by fusing with sodium carbonate and sulphur, and the antimony, if present, determined in the aqueous solution of the melt, as in the case of a complete analysis.

The filtrate from the lead sulphate is treated with 25 c.c. of hydrochloric acid (sp. gr. 1.125), diluted with water to 350 c.c., and a rapid current of sulphuretted hydrogen passed in until the precipitation of the copper is complete; the precipitate is heated to nearly boiling on the water-bath for an hour, the bulky precipitate transferred to an iron-free filter paper and washed well with boiling water. The filtrate must be tested with sulphuretted hydrogen water, to ascertain if any copper remains in solution; after concentrating by evaporation, this

<sup>1</sup> Private communication to Prof. Pufahl.

<sup>2</sup> Fresenius, *Quantitative Analysis*, 7th ed., vol. ii., p. 403.

filtrate serves for the determination of the iron, nickel, and cobalt. The washed precipitate is transferred to a beaker, by means of a bone spatula, and by washing it off the filter paper with a little water; it is then stirred well with solid potassium cyanide until all the copper sulphide is dissolved, giving a pale yellow solution, which is gently warmed and poured through the filter, which still retains a little copper sulphide; if necessary, this residue of copper sulphide must be treated with a little hot potassium cyanide solution. The bismuth sulphide remaining in the beaker and on the filter is washed with hot water, dissolved in warm dilute nitric acid, an excess of ammonia and ammonium sulphide added, and the whole heated for ten minutes in a water-bath; the precipitate is then washed, again dissolved in dilute nitric acid, and the bismuth precipitated as hydroxide by means of ammonia, which is added carefully, drop by drop, to slight excess; any traces of copper remain in solution. The bismuth hydroxide is then dissolved in dilute nitric acid, the solution evaporated to dryness in a porcelain crucible, and the residue converted, by careful heating and ignition, into the oxide and weighed.

*The Colorimetric Estimation of Bismuth*, as described by C. and J. J. Beringer,<sup>1</sup> is rapid and deserves the special notice of technical chemists. It depends on the solubility of the dark brown bismuth iodide,  $\text{BiI}_3$ , in potassium iodide solution, and the gauging of the bismuth content of the intense yellow to brownish yellow solution, after dilution to a specified volume, by comparison with standard solutions of known bismuth content, square containing bottles of the same shape and size being employed.<sup>2</sup> According to the original description, the nitrate solution from 10 g. of copper is neutralised with sodium carbonate, treated with 1 to 1.5 g. of sodium bicarbonate, boiled for ten minutes, the precipitate filtered off, dissolved in hot dilute sulphuric acid, an excess of sulphur dioxide and of an aqueous solution of potassium iodide added, the whole boiled and filtered, and the filtrate diluted to 500 c.c.; 50 c.c. of the yellow solution are compared with the standard solutions.

Pufahl prefers to precipitate the dilute sulphate solution with a slight excess of thiocyanate of potassium, in presence of sulphur dioxide, and then to treat the filtrate from this with 1 or 2 g. of potassium iodide and filter through a double filter; boiling is unnecessary, as is also dilution to 500 c.c. One mg. of bismuth in 500 c.c. shows a distinct yellow coloration. The solutions to be compared must contain free sulphur dioxide. Lead does not interfere, as even considerable amounts of the yellow lead iodide dissolve in potassium iodide to a

<sup>1</sup> *A Text-book of Assaying*, C. and J. J. Beringer, 12th ed., 1910, p. 223-4. Cf. also, *The Colorimetric Estimation of Small Quantities of Bismuth*, this vol., p. 247.

<sup>2</sup> Cf. Heine's *Colorimetric Copper Assay*, this vol., p. 180.



colourless solution. The comparisons should be made either in daylight or in white artificial light; the electric arc light or incandescent gas light may be employed.

A copper solution, free from bismuth, must be used as control; Pufahl at first used copper sulphate, bought as chemically pure, and other preparations, as well as marketable copper, but all were found to contain traces of bismuth.

**Tin.**—This seldom occurs as an impurity in copper; it is separated and determined as described under Complete Analysis, section (a).

**Selenium and Tellurium.**—Small quantities of these elements are frequently found in certain brands of marketable copper. Pufahl examined an "Urmenta" copper, which gave a black deposit of selenium on solution in dilute nitric acid which was at first mistaken for gold; the copper dissolved completely, however, in nitric acid of sp. gr. 1.4. It is possible that the presence of selenium in copper may account for the solution of a small quantity of gold, as it has frequently been noticed that wet methods give lower results than the dry assay for gold in copper.

During the solution of copper for complete analysis by Hampe's method (Complete Analysis, section (b), p. 192), selenium goes into solution as selenic acid,  $\text{H}_2\text{SeO}_4$ , and tellurium as tellurous acid,  $\text{H}_2\text{TeO}_3$ ; both are precipitated quantitatively by the continued action of sulphur dioxide in the warm solution, the deposit consisting of a dark red or blackish powder of the elements. Silver comes down at the same time. Should their presence be indicated in this way, the mixture of selenium, tellurium, and silver is treated with nitric acid, the solution evaporated, the silver precipitated by evaporation with a little hydrochloric acid, filtered off, and the selenium and tellurium precipitated together by warming the solution with a few decigrams of hydroxylamine hydrochloride;<sup>1</sup> the precipitate is collected on a tared filter, then dried for four hours at about  $110^\circ$ , and weighed.

Should more than a few milligrams be present, an approximate separation may be effected by H. Rose's method,<sup>2</sup> as follows:—The material is transferred, as completely as possible, from the filter into a Rose's crucible, and the filter paper re-weighed; the mixture of selenium and tellurium is then fused with at least twelve times its weight of potassium cyanide at a moderate temperature for ten minutes in a current of hydrogen, and the melt allowed to cool in hydrogen, extracted with hot water, the dark red solution of potassium telluride diluted considerably, and the tellurium precipitated, as a black crystalline powder, by passing air through the solution for several

<sup>1</sup> Cf. Keller, "On the Analysis of Refined Copper from Lake Superior," *J. Franklin Inst.*, 1894, 823, 54; *Berg. u. Hütten. Zeit.*, 1894, 53, 410; *J. Soc. Chem. Ind.*, 1895, 14, 303.

<sup>2</sup> Rose-Finkener, *Handbuch d. analytischen Chemie*, vol. ii., p. 431.

hours; the precipitate is collected on a tared filter, dried for four hours at  $100^{\circ}$  to  $110^{\circ}$ , and weighed. Selenium is estimated by difference.

Pufahl is of opinion that there is no advantage in using hydroxylamine, as this precipitates the tellurium only on complete evaporation of the solution, followed by further heating; aqueous sulphurous acid, on the other hand, effects the reduction at once. It is advisable to filter only after continued warming with repeated additions of sulphur dioxide, and to test the filtrate by further warming with sulphur dioxide.

Selenium gives first an orange-yellow turbidity, and then a red precipitate, which gradually becomes reddish black and at the same time covers the tellurium, which is precipitated simultaneously. As a rule, the determination of selenium and tellurium together is sufficient; the total amount of the two in good tough copper rarely exceeds 0.01 per cent.<sup>1</sup> Tellurium, in presence of selenium, may be easily detected qualitatively by gently warming a mixture of the two, in a test tube, with 1 or 2 c.c. of concentrated sulphuric acid; according to von Kobell, the tellurium dissolves first, producing a cherry-red coloration; on stronger heating, this coloration disappears and the presence of selenium is then indicated by the yellowish green colour of the boiling sulphuric acid.

Selenium may be detected also by the characteristic odour produced on burning, and tellurium by the formation of sodium telluride on fusion with sodium carbonate and powdered charcoal; the cooled melt, treated with a little water, gives a purple coloration, which soon becomes turbid with separation of tellurium.

### 3. BLISTER-COPPER (BLACK COPPER)

This is produced in the reducing and smelting of calcined high grade copper matte, and of oxidised copper ores, and also directly from copper matte by the copper Bessemer process; rosette copper, tough copper, or marketable copper is obtained from it by refining.

It is always impure, and contains from 5 to 20 per cent. of foreign elements in variable amounts. Iron and sulphur are always present; in addition, the following may occur: lead, arsenic, antimony, bismuth, zinc, nickel, cobalt, tin, gold, silver, platinum, selenium, and tellurium.

As bars are by no means homogeneous, an average sample is best obtained by drilling completely through a considerable number of bars and mixing the fine drillings well together before weighing out.

The analytical examination is conducted essentially as described under Marketable Copper (Complete Analysis, sections (a) and (b), and also Separate Estimations, pp. 194 *et seq.*). The noble metals

<sup>1</sup> Eggleston found 0.08 per cent. of tellurium in a Colorado copper. As little as 0.03 per cent. in copper produces red-shortness.

are best estimated in the dry way by scorification and cupellation, or by the combined wet and dry method (*cf.* Silver, p. 109).

To determine the sulphur, the drillings are dissolved in strong nitric acid, as described under the sulphur estimation in copper pyrites, p. 184; it is to be borne in mind that lead sulphate may be contained in the insoluble residue, which must, therefore, be extracted with ammonium acetate, and the lead reprecipitated with sulphuric acid (or else as chromate), and the sulphur in the insoluble matter calculated from this result.

For the complete estimation of sulphur, the copper is heated in a current of chlorine, the volatile chlorides being collected in a receiver and treated by the usual methods.

A copper nickel antimoniate is often found in very impure "black copper" containing antimony and nickel, which, when present in considerable quantity, renders the copper unsuitable for refining, except electrolytically. The investigations of Hampe have shown that this compound has the composition  $6\text{Cu}_2\text{O} \cdot \text{Sb}_2\text{O}_5 + 8\text{NiO} \cdot \text{Sb}_2\text{O}_5$ ; it is decomposed by fusion with sodium carbonate and sulphur, or with acid potassium sulphate.

#### 4. CEMENT COPPER (COPPER PRECIPITATE)

Copper precipitate, produced from copper liquors and mine liquors, by means of iron (pig iron, scrap, and spongy iron), is usually moist and contaminated by many foreign metals, and also by arsenic, antimony, basic salts of iron, etc.

Sampling may be effected by taking a considerable quantity from a large number of bags, so that the total amount is, say, 25 kg.; this is sieved through various sized metal sieves, loss through dusting being avoided, so that three or four different products are obtained, portions of each of which are taken, in the ratios of their respective weights, so that ultimately a sample of from 100 to 200 g. is obtained for analysis.

For the analysis, a solution of 100 g. is prepared and diluted to 2 litres; in one portion of the solution copper, bismuth, arsenic, antimony, lead, and iron are determined, according to the methods described for marketable copper; the noble metals are assayed in the dry way.

Moisture is determined on a separate sample, of several hundred grams by heating to  $100^\circ$ .

Chlorine is determined by boiling 50 g. with about 300 c.c. of very dilute nitric acid (one volume sp. gr. 1.2 to ten volumes water), filtering, and precipitating a tenth part of the filtrate with silver nitrate.

#### 5. COPPER SCALE, SWEEPINGS, AND RESIDUES

In the absence of dirt, particles of wood, etc., the material is crushed, and a large sample, weighing several kilograms, sieved through metal



sieves of various mesh, and proportional parts are mixed, from which a sample of about 50 g. is weighed out; pieces of iron are removed with a magnet. The remainder is warmed for an hour in a covered porcelain dish on a water-bath with 300 c.c. of ordinary hydrochloric acid, 30 c.c. of nitric acid (sp. gr. 1.2) being added, little by little; as soon as effervescence has ceased, the solution is cooled, diluted, and washed into a litre flask; 50 c.c. are then withdrawn, evaporated down with 5 c.c. of sulphuric acid, the residue taken up with water, a little nitric acid added to the solution, and the copper deposited electrolytically on a cone. The filtered sulphate solution may also be precipitated with sodium thiosulphate, and the sulphide dissolved and determined volumetrically.

Clean copper scale may be dissolved in concentrated nitric acid, and the solution, after dilution, electrolysed.

Sweepings containing organic matter are first burnt, then sieved, and, when any amount of metallics is visible, the material is then warmed for one or two hours with nitric acid, a little hydrochloric acid being also added. The solution is then diluted considerably, and so much taken as corresponds to from 2 to 2.5 g. of material; this is evaporated with sulphuric acid and treated as usual. Should the material consist almost entirely of oxides, it is dissolved in hydrochloric acid, with the addition of a little nitric acid.

#### 6. PHOSPHOR-COPPER, SILICON-COPPER, AND MANGANESE-COPPER

Phosphor-copper is principally added to bronze alloys as a deoxidising agent, in place of red phosphorus; silicon-copper is used in the manufacture of silicon bronze (for telegraph wires, etc.); manganese-copper is employed in the manufacture of manganese-zinc-copper alloys, such as delta-metal, etc. They are made, as a rule, from very pure copper.

All these alloys are brittle and easily reduced to powder; they are analysed in the form of very fine powder.

**Phosphor-copper.**—This contains up to 20 per cent. of phosphorus.

*Determination of Phosphorus.*—Half a gram of the very finely powdered material is heated for a considerable time in a porcelain dish, over a very small flame, with 10 c.c. of nitric acid (sp. gr. 1.4); if, at the end of half an hour, any material be still undissolved, a few drops of hydrochloric acid are gradually added, in which case the solution obtained is evaporated with 10 c.c. of ordinary nitric acid. (Phosphor-copper dissolves more rapidly in aqua regia, but a considerable amount of phosphorus volatilises as chloride.) The residue from the evaporation is taken up with a little nitric acid and water, any silica filtered off, ammonia added in excess, and the phosphoric acid precipitated with magnesia mixture. Traces of copper in the double-salt have practically

no influence on the result, the washed ammonium magnesium phosphate may, however, be dissolved in dilute hydrochloric or nitric acid, and reprecipitated pure by the addition of a little magnesia mixture. The precipitate is converted into magnesium pyrophosphate, and weighed.  $\text{Mg}_2\text{P}_2\text{O}_7 \times 0.2784 = \text{P}$ .

Pufahl prefers to precipitate the phosphoric acid with molybdate, and then to further treat the precipitate by R. Finkener's method.<sup>1</sup> One-fifth of the solution of 0.5 g. of material is concentrated to about 10 c.c. by evaporation in a porcelain dish of 250 c.c. capacity, 150 c.c. of molybdate solution, prepared according to Finkener's instructions (see below), added, and as much ammonium nitrate as will dissolve in the cold; the phosphoric acid is precipitated quantitatively, as ammonium phospho-molybdate, in from twelve to eighteen hours. The precipitate is filtered through a stout filter paper which has been moistened with concentrated ammonium nitrate solution, and is washed with a 20 per cent. solution of ammonium nitrate, containing a little nitric acid; a single final washing may be given with 5 per cent. nitric acid (5 c.c. nitric acid of sp. gr. 1.2 in 100 c.c.). The precipitate is washed, by means of as little water as possible, into a weighed porcelain crucible, which is then placed on a water-bath and heated to boiling; any precipitate remaining on the sides of the dish and on the filter paper is dissolved in a little dilute ammonia, the filter washed three times with a little water, and the solution and washings evaporated in a porcelain crucible on the water-bath. Should the volume be only a few cubic centimetres, a drop of ammonia is added, and the solution transferred to the weighed porcelain crucible by the aid of a few drops of water; after the addition of a few drops of nitric acid, the solution is evaporated to dryness on the water-bath. In order to drive off the ammonium nitrate and to convert the phospho-molybdate into a weighable phosphorous compound, the crucible is heated on a sand-bath, the temperature being gradually increased, until a watch-glass, laid on the crucible for an hour, no longer shows a sublimate of ammonium nitrate; strong heating is not necessary. Should a portion of the yellow salt become greenish black through too strong heating, with consequent partial reduction of the molybdic acid, this has no appreciable effect on the result. The crucible, while still warm (over  $100^\circ$ ), is put into a desiccator over sulphuric acid to cool for half an hour, and is weighed, covered. Or, the molybdate precipitate may be filtered on to a tared filter paper, dried, and weighed. The yellow salt contains 3.753 per cent. of phosphorous pentoxide, or 1.639 per cent. of phosphorus.

The molybdate solution is prepared as follows:—Eighty grams of ammonium molybdate are shaken with 640 c.c. of water and 160 c.c.

<sup>1</sup> *Ber.*, 1878, **11**, 163; *J. Chem. Soc. Abstr.*, 1879, **36**, 275.

of ammonia (sp. gr. 0.925) in a flask until dissolved, and this solution poured in several portions, with continuous stirring, into a well-cooled mixture of 960 c.c. of nitric acid (sp. gr. 1.18) and 240 c.c. of water; the clear solution is syphoned off and kept in a stock-bottle, covered with a beaker or other loose cover; if kept in a tightly stoppered bottle, considerable quantities of a yellow acid ammonium molybdate soon begin to separate.

Excess of this solution must be employed for the precipitation, so that, as Finkener states, not more than two-thirds of the quantity added will be actually required to form the yellow precipitate.

If arsenic acid be contained in the assay solution, this comes down in the main as ammonium arseno-molybdate; dissolved silica is also precipitated; these must, therefore, be both removed beforehand (*cf.* Separate Estimations, Phosphorus, p. 195).

*Determination of Copper.*—One gram of the fine powder is dissolved in a covered porcelain dish by means of a mixture of 10 c.c. of nitric acid (sp. gr. 1.2) and 5 c.c. of ordinary 25 per cent. hydrochloric acid, the solution evaporated down with 1 to 2 c.c. of distilled sulphuric acid, 10 c.c. of water added, and the evaporation repeated; the residue is then dissolved in water and electrolysed, after acidifying with nitric acid.

**Silicon-Copper.**—This usually contains about 12 per cent. of silicon. For the analysis, 1 g. of the finely powdered material is heated for some time in a covered porcelain dish with 10 to 20 c.c. of nitric acid (sp. gr. 1.4), finally 1 to 2 c.c. of hydrochloric acid added, the mixture again warmed, then evaporated with 2 c.c. of sulphuric acid, and the residue heated until sulphuric acid vapours are given off; the silica is thus rendered insoluble. The residue is taken up with water, the solution warmed, the silica filtered off, washed with hot water, and the copper precipitated from the filtrate. The filter paper with the silica is burnt wet in a platinum crucible and finally ignited strongly. After being weighed, the silica is tested as to purity, by dissolving it in 10 c.c. of pure hydrofluoric acid and a drop of sulphuric acid, the solution evaporated, the evaporation repeated with sulphuric acid, and any residue of copper oxide strongly heated in presence of air, and weighed.  $\text{SiO}_2 \times 0.4693 = \text{Si}$ .

**Manganese-Copper.**—The manganese content varies, and may be as high as 40 per cent. The products of the Isabellenhütte, in Nassau, for instance, contain 4, 10, 15, and 30 per cent. of manganese, and are respectively copper-red, reddish grey, yellowish grey, and grey in colour. Sampling is effected by drilling a few ingots and mixing the fine drillings thoroughly. Manganese-copper always contains a little iron (1 to 2 per cent.), a little silicon, and the impurities from the copper used.

The analysis is carried out as follows:—One gram of drillings is dis-



solved in a covered porcelain dish, in 10 to 15 c.c. of dilute nitric acid, the solution evaporated with 2 c.c. of sulphuric acid, the silica rendered insoluble by further heating, the cooled residue then warmed with sulphuric acid and water, the solution filtered, and the silicon determined as in the case of silicon-copper; any lead is retained as lead sulphate with the silica, and is dissolved out by treatment with a hot solution of ammonium acetate. The filtrate is diluted to 400 or 500 c.c., a few cubic centimetres of sulphuric acid added, the copper precipitated by passing sulphuretted hydrogen into the warm solution, the precipitate of copper sulphide washed with water containing a little sulphuric acid and sulphuretted hydrogen, and either converted into sulphide by Rose's method (p. 169), or dissolved in nitric acid, and the solution electrolysed (p. 163). The filtrate from the copper sulphide is evaporated in a porcelain dish, and, after the sulphuretted hydrogen has been driven off, oxidised with a few drops of bromine water and concentrated to about 200 c.c.; the cooled solution is made up to 300 c.c. in a graduated flask, and one-third of this taken for the estimation of the iron, by reduction with amalgamated zinc and titration with potassium permanganate; the remaining two-thirds are used for the determination of the manganese by titration with permanganate (Volhard's method, pp. 34 *et seq.*). The results of two analyses by Pufahl are given in the following table:—

	Cu.	Mn.	Si.	Fe.	Ni.	Pb.
(a)	68.39	29.94	0.07	1.29	0.19	0.06
(b)	56.29	40.86	1.08	1.5	0.1	trace

#### 7. ALLOYS OF COPPER WITH TIN, ZINC, LEAD, IRON, MANGANESE, AND NOBLE METALS<sup>1</sup>

Copper alloys are always either attacked or dissolved by nitric acid; alloys rich in tin are analysed in the form of turnings or flattened chippings.

##### (a) Bronzes

(Bell metal, gun metal, phosphor-bronze, phosphor-lead bronze, machine brasses, manganese bronze, statuary and medallion bronzes, silicon-bronze.)

One gram of drillings is treated with 10 c.c. of pure nitric acid (sp. gr. 1.4) in a covered round-bottomed porcelain dish, standing in cold water; or a platinum dish, of about 300 c.c. capacity and completely covered with a clock-glass, may be used for the purpose. At the end of half an hour the dish is heated on a water-bath, and, after nitrous fumes

<sup>1</sup> For copper-nickel alloys and German silver, see Nickel; for white metals (anti-friction alloys) and britannia metal, see Tin; for aluminium bronzes, see Aluminium.

have disappeared, 100 c.c. of hot water are added, and the whole boiled for five minutes over a free flame; the metastannic acid is filtered off on a stout ash-free paper, washed with hot water, dried, the filter paper burnt and put into a porcelain crucible; the precipitate itself is then added, and the whole strongly ignited for ten minutes, allowed to cool in a desiccator for half an hour, and weighed.  $\text{SnO}_2 \times 0.7881 = \text{Sn}$ .

The filtrate from the metastannic acid is evaporated on a water-bath, in a flat porcelain dish of about 15 cm. diameter, with 2 c.c. of sulphuric acid, the residue dissolved in 30 c.c. of water, the dish cooled by floating it on cold water, the lead sulphate filtered off at the end of an hour on a small filter, washed several times with water containing a little sulphuric acid (0.5 c.c. acid to 100 c.c. water), and finally with pure water, then dried, and the paper incinerated at a low temperature in a porcelain crucible; if lead prills are formed, the residue is warmed with a little dilute nitric acid on the water-bath, a drop of sulphuric acid added, the excess of acid evaporated off, and the residue ignited. The larger portion of the lead sulphate is previously transferred from the filter paper to a sheet of glazed paper, and is now added to the contents of the crucible.  $\text{PbSO}_4 \times 0.6831 = \text{Pb}$ .

The filtrate from the lead sulphate is transferred to a platinum crucible, of about 150 c.c. capacity, treated with 5 c.c. of sulphuric acid and 0.2 to 0.5 c.c. of nitric acid (sp. gr. 1.2), and the copper determined electrolytically. The copper is completely deposited in from six to seven hours, or, at all events, only a minute quantity, seldom amounting to more than a milligram, remains in solution at the end of this time.

The solution from the deposition of the copper is warmed, sulphuretted hydrogen passed in, any copper sulphide filtered off through a small filter, washed with hot water, as the copper sulphide obtained does not oxidise readily, and ignited in air; the small quantity of copper sulphide is converted into the oxide, which is weighed.  $\text{CuO} \times 0.7989 = \text{Cu}$ .

If the total amount of metals found as copper, tin, and lead amounts to approximately 100 per cent., the filtrate from the copper sulphide may be evaporated down over a small flame, for the estimation of any iron and nickel. The sulphuric acid is evaporated off, without the solution being allowed to boil, and the residue ignited; should this consist merely of a reddish skin of ferric oxide, it is dissolved by warming with a little hydrochloric acid, the solution diluted with from 20 to 30 c.c. of water, warmed to about 70°, a little potassium iodide added, and, after stirring well, with the addition of 5 c.c. of carbon bisulphide, the solution is allowed to stand for half an hour, and the free iodine titrated with standard sodium thiosulphate. Should the above residue, however, consist in part of compact pieces, small quantities of zinc and nickel may be present in addition to iron, in which case it is dissolved in a few cubic centimetres of hydrochloric acid, evaporated with a few

drops of sulphuric acid, the residue taken up with water, and the zinc precipitated as sulphide by means of a current of sulphuretted hydrogen, which is passed for some time through the diluted solution, after neutralising with sodium carbonate (using Congo red paper as indicator), and then slightly acidifying with sulphuric acid (*cf.* Zinc). The filtrate is boiled in a porcelain dish, excess of bromine water added, the nickel and iron precipitated with sodium hydroxide, and the precipitate filtered, washed, and ignited; the mixed oxides of iron and nickel are weighed, then dissolved in hydrochloric acid, the iron estimated volumetrically as above and calculated to ferric oxide, and the nickel oxide estimated by difference.  $\text{NiO} \times 0.7858 = \text{Ni}$ .

Instead of the foregoing, the iron may be precipitated from the iron and nickel solution as basic acetate, and the nickel determined in the filtrate by precipitation with sodium hydroxide and bromine water, and weighed as oxide.

Should a separate determination of nickel not be required (it seldom amounts to more than 0.2 per cent.), the method may be simplified by adding a slight excess of sodium carbonate to the dilute hydrochloric acid solution of the ignited residue, boiling for five minutes, filtering off the impure basic zinc carbonate, washing with hot water, and drying; the precipitate is then transferred to a porcelain crucible, after the filter paper has been burnt and ignited, so as to convert it into impure zinc oxide (containing iron and probably nickel), and weighed; the oxides are dissolved in a little hydrochloric acid, the iron titrated as above, calculated to ferric oxide, and subtracted from the above weight.  $\text{ZnO} \times 0.8034 = \text{Zn}$ .

**Bronzes which contain Zinc.**—(Machine brasses, bearing metals, statuary and medallion bronzes.)

When the total of copper, tin, and lead leaves a deficit of over 1 per cent. (zinc), the zinc is precipitated by means of sulphuretted hydrogen from the diluted solution, which must be very slightly acid with a mineral acid, and the zinc sulphide weighed (*cf.* Zinc). Iron and nickel are precipitated together in the filtrate from the zinc sulphide and are determined as described above.

The presence of manganese, which is introduced as manganese-copper into some copper-tin-zinc alloys, such as manganese bronze, is indicated by the violet colour of the liquid at the anode, during the electrolytic deposition of the copper, and also by the separation of a flocculent precipitate of hydrated peroxide of manganese. If present, the solution, after the separation of the copper, is evaporated down, the greater part of the sulphuric acid removed by evaporation, the residue diluted, neutralised with sodium hydroxide, the zinc precipitated with sulphuretted hydrogen, and the manganese and iron precipitated together in the filtrate from the zinc sulphide by means of sodium



hydroxide and bromine water; this precipitate is washed, the hydroxides, which still retain alkali, dissolved in the smallest possible quantity of hydrochloric acid with addition of a few drops of an aqueous solution of sulphur dioxide, excess of ammonia added, and then a few drops of pure hydrogen peroxide; after heating for a short time, the precipitate is filtered off, dried, ignited strongly in an open porcelain crucible, and weighed as  $\text{Mn}_3\text{O}_4 + \text{Fe}_2\text{O}_3$ . The oxides are then dissolved in hydrochloric acid and the iron titrated, the corresponding amount of ferric oxide being subtracted from the weight of the mixed oxides.  $\text{Mn}_3\text{O}_4 \times 0.7203 = \text{Mn}$ .

A more accurate determination of the manganese, which is usually very small in amount, is seldom necessary. If required, however, the iron is precipitated from the solution of the two oxides as basic acetate, and the manganese precipitated from the filtrate by adding bromine water in excess to the cold solution, followed by an excess of ammonia and boiling; the precipitate is allowed to settle, filtered, washed with hot water, dried, ignited, and weighed as  $\text{Mn}_3\text{O}_4$ .

The following rapid method for the analysis of bronzes and bearing metals has been worked out by M. E. Walters and O. L. Affelder<sup>1</sup>:—

*Bronzes*.—One gram of material (or, if the lead content is over 15 per cent., only 0.5 g.) is decomposed by warming with 10 c.c. of nitric acid (sp. gr. 1.42), 40 c.c. of hot water added, and the whole boiled for five minutes. The precipitated oxide of tin is washed with 2 per cent. nitric acid, ignited, and weighed. To the filtrate 25 c.c. of strong ammonia are added, the solution heated to boiling, then 5 g. of ammonium persulphate added, and the boiling continued for five minutes; after acidifying with sulphuric acid, the precipitated lead peroxide is filtered off, washed with hot water, the precipitate and filter transferred to a beaker, well agitated, 600 to 700 c.c. of cold water added, and then about 3 g. of potassium iodide, and starch. After the potassium iodide has dissolved, 10 c.c. of hydrochloric acid (1 to 1) are added, the whole well stirred and titrated with  $N/20$  thiosulphate solution, until the colour changes from dark to very pale yellow; the number of cubic centimetres of thiosulphate solution used, multiplied by 0.5178, gives the percentage of lead. The lead may also be determined gravimetrically.

The filtrate from the lead peroxide is diluted to 500 c.c., heated to boiling, and treated with 50 c.c. of a 20 per cent. sodium thiosulphate solution, for precipitation of the copper; the precipitate is washed with hot water, dissolved, and the copper determined volumetrically. In the filtrate from the copper precipitate, the iron and aluminium are determined as usual, and then the manganese precipitated by boiling the ammoniacal solution with ammonium persulphate.

Excess of ammonium phosphate is added to the filtrate from the

<sup>1</sup> *J. Amer. Chem. Soc.*, 1903, 25, 632; *Z. angew. Chem.*, 1903, 16, 1081.

manganese precipitate, the liquid heated to boiling, hydrochloric acid added gradually until only a slight smell of ammonia can be detected, the whole then boiled for several minutes, filtered, the precipitate washed with hot water, and then dried at  $100^{\circ}$  to  $105^{\circ}$  and weighed as zinc ammonium phosphate,  $\text{ZnNH}_4\text{PO}_4$ ; <sup>1</sup> or, it may be ignited and weighed as zinc pyrophosphate,  $\text{Zn}_2\text{P}_2\text{O}_7$ .

Any nickel is precipitated as sulphide in the filtrate from the zinc precipitate.

Small quantities of manganese may be estimated colorimetrically in a separate sample.

Phosphorus is precipitated as ferric phosphate in a separate sample, dissolved in nitric acid, lead, tin, and copper being first precipitated by metallic zinc; the phosphorus is then determined in the ferric phosphate by the molybdate method.

*Bearing Metals.*—These usually contain antimony. The antimony and tin are first determined together as oxides,  $\text{Sb}_2\text{O}_3 + \text{SnO}_2$ , as described above, and the antimony determined in a separate sample as sulphide, either by Andrews' method <sup>2</sup> or as metal. Tin and antimony in bearing metals are also often determined volumetrically. Arsenic is determined in a separate portion by the distillation method. Other metals are determined as in the analysis of bronzes.

If bismuth be present, it can be precipitated with the copper as sulphide, and then separated by dissolving in nitric acid and precipitating with ammonia.

The presence of manganese is very quickly detected by decomposing a few decigrams of the alloy in a test tube with a little nitric acid, boiling off nitrous fumes, diluting with water, adding dilute silver nitrate solution, and a small quantity of solid ammonium persulphate; on warming, a violet coloration, due to permanganic acid, is obtained.

**Impurities in the Stannic Acid and their Determination.**—A yellowish or brownish coloration of the metastannic acid indicates contamination with ferric oxide; other possible impurities are antimonious and phosphoric acids and traces of cupric oxide.

As a rule, in technical work, it is sufficient to test qualitatively for arsenic and antimony. This is effected by fusing the stannic acid until the melt is tranquil with about 2 g. of potassium hydroxide in an iron or nickel spoon 35 mm. in diameter, 10 mm. deep, and provided with a handle 150 mm. long; the fusion is carried out over a large Bunsen burner and the precaution taken to wrap the hand in a towel and to keep the face turned away. When the melt has cooled, it is dissolved by stirring for a few minutes in a beaker with about 25 c.c. of water, the solution treated with 25 c.c. of pure 25 per cent. hydrochloric acid and tested in a simple form of Marsh's apparatus, employing pure

<sup>1</sup> *Z. anal. Chem.*, 1900, 39, 273.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1895, 17, 872.

granulated zinc; a large test tube (180 mm. long and 30 mm. wide) serves the purpose quite well. About 10 g. of pure zinc are first introduced, followed by the solution to be tested, then a plug of cotton wool 30 to 40 mm. thick inserted, and finally a rubber stopper, provided with a short glass tube drawn out to a jet, on to which the platinum nozzle of a blowpipe is fixed. A glazed porcelain plate is held in the hydrogen flame, on which a series of deposits are produced in the usual way; 1 mg. of arsenic or antimony produces an immediate brown to dull black spot on the plate. Brown arsenic sublimates disappear immediately on treatment with a solution of sodium hypochlorite; antimony sublimates are practically unaffected. If similar deposits are made by using solutions containing known amounts of arsenic and antimony, it is possible to say, from the character of the sublimate obtained, whether more than a trace or over one-tenth per cent. of these impurities is present in the alloy under investigation.<sup>1</sup>

Should notable amounts of antimony and lead be found in bronze, it is probable that scrap metal has been used in the manufacture, such as, for instance, turnings from bearing metals, rendered impure by a coating of white metal. Bronzes made from the best materials should contain very little lead (0.1 to 0.2 per cent.), due to the lead contained in commercial zinc, and traces only of arsenic and antimony.

For the quantitative estimation of the impurities, the stannic acid is fused in a porcelain crucible with six times its weight of a mixture of equal parts of sodium carbonate and sulphur (or the same quantity of dehydrated sodium thiosulphate), the melt extracted with hot water and the solution filtered; copper, iron, and any small quantity of lead remain on the filter paper as sulphides, whilst tin, arsenic, and antimony go into solution as sulpho-salts. The sulphides of iron and lead are dissolved by dropping hot dilute hydrochloric acid on to the filter; copper sulphide remains undissolved. The lead is separated by evaporating with a few drops of sulphuric acid, and the iron precipitated from the filtrate with ammonia, after the addition of a little bromine water, and either weighed as ferric oxide, after ignition, or determined volumetrically. The small quantity of copper sulphide, after being washed, is converted into cupric oxide by ignition in a platinum crucible, and weighed. The dark yellow solution of the sulpho-salts is treated according to Hiepe's method.<sup>2</sup> It is heated to boiling with pure sodium hydroxide solution, and small quantities of a solution of hydrogen peroxide added little by little, but not to complete decolorisation; by this means the sulphur, in excess of that contained as sodium sulphide, is oxidised as far as possible; should the decolorisation have become

<sup>1</sup> The methods for the detection and approximate estimation of small quantities of arsenic are fully described in Vol I., pp. 362 *et seq.*

<sup>2</sup> *Chem. Zeit.*, 1889, 13, 1303; *J. Soc. Chem. Ind.*, 1890, 9, 109.



complete, a slight addition of sodium sulphide is necessary before the precipitation of the sulphides with sulphuric acid. The solution is acidified with sulphuric acid, heated for some time to drive off sulphuretted hydrogen, and the precipitated sulphides, which now contain only traces of free sulphur, filtered off and washed with hot water containing a little ammonium acetate and acetic acid. The sulphides are then dissolved in hydrochloric acid and potassium chlorate, fuming hydrochloric acid added, and the arsenic precipitated by passing sulphuretted hydrogen for a considerable time; the filtrate from the sulphide of arsenic is warmed with a little bromine water, and the tin and antimony separated in the solution, after a certain amount of dilution, by means of pure iron (*cf.* Analysis of White Metal, p. 258). The antimony is ultimately weighed as tetroxide,  $\text{Sb}_2\text{O}_4$ , and the arsenic as magnesium pyroarsenate,  $\text{Mg}_2\text{As}_2\text{O}_7$  (*cf.* Arsenic, p. 272). Phosphorus, if contained in the alloy, is estimated in a separate sample (*cf.* Phosphor-Bronze), and the corresponding amount of phosphoric acid deducted from the impure stannic acid, although the phosphoric acid does not come down quantitatively with the stannic acid. The result obtained by weighing the pure stannic oxide, obtained finally from the filtrate from which antimony has been precipitated by iron, is more accurate than that arrived at by subtracting the weight of foreign oxides from the weight of impure stannic oxide, and so estimating the pure stannic oxide by difference.

This lengthy and tedious process is naturally only employed when an accurate analysis of the bronze is required. In this case, about 1 g. of the alloy is first tested for arsenic and antimony by dissolving it in 20 c.c. of pure hydrochloric acid and a little potassium chlorate, diluting to 50 c.c., and testing in a simple form of Marsh's apparatus; should the presence of arsenic and antimony be proved qualitatively, the impure stannic oxide is fused, and the analysis conducted as described.

**Phosphor-Bronze.**—The method of analysis is the same as that for ordinary bronze; the phosphorus is estimated in a separate sample. The method employed by Pufahl<sup>1</sup> is as follows:—One gram of fine drillings is treated in a deep, covered porcelain dish of about 10 cm. diameter, with 7 c.c. of nitric acid (sp. gr. 1.4); after standing for five minutes, the dish is placed on a water-bath, heated to boiling, at the end of ten minutes the cover-glass removed, and the free acid evaporated off. The residue is stirred with 10 c.c. of hydrochloric acid, again evaporated to dryness, the brown residue dissolved by warming with 10 c.c. of dilute nitric acid, the dish removed from the water-bath, and 50 c.c. of molybdate solution and 15 g. of solid ammonium nitrate added; the whole is well stirred until the ammonium nitrate has dissolved. The yellow precipitate of ammonium phospho-molybdate is

<sup>1</sup> *Cf.* Kerl, *Fortschritte in der Metallurgischen Probierkunst*, 1887, p. 92.

filtered off, after standing for twelve hours, and treated by Finkener's method, as described under Phosphor-Copper, p. 206.

Small quantities of the yellow precipitate (from bronze containing at most 0.2 per cent. of phosphorus), are dissolved off the filter with dilute ammonia, the filter paper washed with a little water, the solution evaporated down to from 1 to 2 c.c. in a tared porcelain crucible of 50 mm. diameter, a drop of ammonia added, the crucible shaken round, and the phospho-molybdate reprecipitated with 1 to 2 c.c. of nitric acid; the whole is then taken to dryness and the ammonium nitrate removed by heating on a sand-bath (*cf.* Phosphor-Copper).

Should the phosphor-bronze contain arsenic, which is seldom the case, since specially pure copper is used in its manufacture, the brown residue is taken up with hydrochloric acid and water, the solution diluted to 500 c.c., warmed, then sulphuretted hydrogen passed in, the bulky precipitate, containing copper, tin, arsenic, and probably lead, filtered off and the filtrate evaporated to dryness; the residue is washed into a small dish of 10 cm. diameter, evaporated with 10 c.c. of nitric acid, and the phosphoric acid precipitated as before with molybdate solution.

The same procedure is followed in estimating the phosphorus in bronzes containing much lead. A phosphor-lead bronze is largely used for bearings, especially in the United States. The average composition of the alloy used by the Pennsylvania Railroad Co. is:—

Cu	.	.	.	79.7 per cent.
Sn	.	.	.	10.0 „
Pb	.	.	.	9.5 „
P	.	.	.	0.8 „

In Kühne's phosphor-lead bronze, Pufahl found:—

Cu	.	.	.	78.01 per cent.
Sn	.	.	.	10.36 „
Pb	.	.	.	10.45 „
Fe	.	.	.	0.09 „
Ni	.	.	.	0.26 „
P	.	.	.	0.57 „

This is identical with the American alloy.<sup>1</sup>

**Silicon-Bronze.**—This alloy contains very little silicon, and frequently small quantities of tin and zinc; it is chiefly used in the manufacture of telegraph and telephone wires.

As in the analysis of bronze, 1 g. is decomposed with 10 c.c. of nitric acid (sp. gr. 1.4), 100 c.c. of hot water added, the whole boiled for five minutes, and the siliceous stannic acid filtered off. The filter is incinerated in a platinum crucible, the stannic acid then added, and the

<sup>1</sup> A number of analyses are given in Muspratt-Stohmann's *Handbuch der technischen Chemie*, 4th ed., vol. iv., in the section on Copper.

whole ignited and weighed; one drop of sulphuric acid and 2 c.c. of pure hydrofluoric acid are added, the liquid evaporated on the water-bath, the sulphuric acid driven off, and the pure stannic oxide weighed, after ignition; the loss in weight gives the silica.

For the determination of the dissolved silica, the filtrate from the stannic acid is evaporated to dryness with 3 c.c. of sulphuric acid, the residue heated to drive off sulphuric acid, water added, and the silica, which may contain a trace of lead sulphate, filtered off, washed with water, treated with a hot dilute solution of ammonium acetate, and a few drops of a solution of potassium chromate added to the filtrate so obtained; any lead chromate precipitated is collected on a tared filter, and dried at 100°. The filter paper, with the silica, is incinerated and weighed.  $\text{SiO}_2 \times 0.4693 = \text{Si}$ .

Copper is deposited electrolytically in the filtrate from the silica. The residual solution is then evaporated, sulphuric acid removed by heating, and the iron and zinc determined as described in the section on Bronze Analysis, p. 211.

If the silica only is to be determined, the sample may be dissolved in aqua regia, the solution evaporated to dryness, and then again evaporated twice successively with 15 c.c. of hydrochloric acid; the residue is heated to 120°, allowed to cool, moistened with fuming hydrochloric acid, then treated with water and the silica filtered off and washed, etc. After being weighed, it is tested for impurities by evaporation with a little hydrofluoric acid and one drop of sulphuric acid, as above.

The following are two analyses, by Hampe, of Weiller's patent silicon-bronze :—

	Telegraph wire.	Telephone wire.
Cu	99.94	97.12 per cent.
Sn	0.03	1.14 „
Fe	trace	trace
Zn	...	1.62 „
Si	0.02	0.05 „

### (b) Brass and similar Alloys.

[Brass, yellow metal, tombac, red brass, aluminium brass, Muntz metal, Aich metal, sterro-metal, delta-metal, Dutch metal, bronze powder, hard solder, white brass, button metal, etc.]

These alloys contain copper and zinc as their principal constituents, and, in addition, either merely the impurities of the copper and zinc, or specially added, tin, iron, manganese, lead, or aluminium.

In the case of alloys not containing tin, 1 g. is dissolved in a



covered porcelain dish on a water-bath, in 10 to 15 c.c. of nitric acid (sp. gr. 1.2), the solution evaporated to dryness with the addition of 5 c.c. of 50 per cent. sulphuric acid, the residue taken up with 30 c.c. of water, and cooled, and the lead sulphate collected on a small filter. The copper is deposited electrolytically in a platinum crucible. The solution from the copper estimation is neutralised with ammonia in a large beaker of 500 c.c. capacity, kept cool with water; it is then slightly acidified with sulphuric acid, diluted to 400 c.c., sulphuretted hydrogen passed in for two or three hours, and the zinc sulphide filtered off after standing for twelve hours (*cf.* Zinc).

The filtrate from the zinc sulphide is evaporated to about 100 c.c., and the iron oxidised with a few drops of bromine water, the excess of bromine boiled off, the cooled solution neutralised, and the iron and aluminium (in aluminium brass) precipitated by ammonium acetate and boiling; the manganese is precipitated in the filtrate in the usual way with ammonia and ammonium sulphide. The iron and aluminium precipitate is dried, the filter paper burnt in a platinum crucible, the main bulk of the precipitate being added subsequently, and the whole strongly ignited and weighed. (The presence of an appreciable amount of alumina is indicated by a light red colour of the oxides.) The oxides are then fused with six times their weight of acid potassium sulphate, the cooled melt dissolved in dilute hydrochloric acid, and the iron and alumina separated by potassium hydroxide in the usual way.  
 $\text{Al}_2\text{O}_3 \times 0.5303 = \text{Al}.$

It is much more convenient to estimate the alumina in the mixture by difference, by dissolving the melt in the crucible in hot dilute sulphuric acid, washing the solution into an Erlenmeyer flask, then reducing the iron by means of amalgamated zinc and titrating the ferrous sulphate with standard potassium permanganate.

The following method can be recommended as a satisfactory works' process:—The solution of the alloy and the precipitation of the lead are effected as above; the copper is deposited electrolytically, and then an excess of ammonia added to the residual solution, whereby a yellowish coloration is produced if traces only of iron be present, or a precipitate of ferric hydroxide if there is an appreciable amount; in the latter case the iron is subsequently estimated volumetrically. (Certain classes of brass, such as cartridge brass, for instance, must be of absolutely definite composition, and may contain only very little lead and traces of iron.) The precipitation of the copper may be more rapidly effected (from, say, one-third of the filtrate from the lead sulphate) by means of sodium thiosulphate, after strongly acidifying with sulphuric acid (*cf.* p. 170), and the copper sulphide converted into cupric oxide by roasting. The percentage of zinc is ascertained by difference.

Alloys which contain tin (certain brands of cartridge brass, red

brass, bronze powder, hard solder, etc.) are analysed in the same way as bronze.

Even minute quantities of antimony contained in the copper produce cold-shortness in brass, and the resulting alloy is consequently unsuitable for rolling; for this reason electrolytic copper, which frequently contains antimony, is seldom used by brass manufacturers. According to the investigations of E. S. Sperry,<sup>1</sup> best brass for cold rolling should not contain over 0.01 per cent. of antimony. Bismuth is just as injurious; arsenic is less so, in fact, thin sheets are frequently met with, containing as much as 0.1 per cent. of arsenic.

### (c) Alloys of Copper with Gold and Silver.

For the determination of the noble metals, *cf.* Gold (pp. 134 *et seq.*) and Silver (pp. 110 *et seq.*).

1. *Gold-Copper Alloys*.—The flattened alloy is dissolved in aqua regia, the solution evaporated, and the residue digested with water and a few drops of hydrochloric acid; the resulting solution is diluted and, after standing for several hours, any silver chloride filtered off on a small filter. The gold is precipitated in the filtrate by adding an excess of pure oxalic acid<sup>2</sup> to the hot dilute solution; the carbon dioxide is driven off by boiling, the solution carefully neutralised with pure alkali, and the deep blue solution of copper potassium oxalate filtered off; the gold is thus obtained free from copper oxalate. The copper is precipitated by boiling the filtrate from the gold with potassium or sodium hydroxide; the precipitate is filtered off, washed, dried, ignited, and weighed.

If impurities contained in the alloy are to be estimated, the gold is precipitated by passing sulphur dioxide into the heated dilute hydrochloric acid filtrate from the silver chloride, the filtrate from the gold boiled to remove sulphur dioxide, then oxidised with a little nitric acid and evaporated with sulphuric acid; any lead sulphate is filtered off and the copper deposited electrolytically and tested for bismuth, which is estimated, if present (*cf.* Analysis of Marketable Copper, pp. 199 *et seq.*). The solution from the deposition of the copper is evaporated down, the sulphuric acid driven off, and the iron, nickel, etc., which are present usually in traces, estimated in the residue (*cf.* Analysis of Bronze, p. 208).

2. *Silver-Copper Alloys*.—(Coinage alloys, silver-plate, silver solder, and bronze powder containing silver, copper, and zinc; coins containing copper, silver, zinc, and nickel, etc.)

The alloy is dissolved in nitric acid, the solution diluted largely,

<sup>1</sup> *Trans. Amer. Inst. Min. Eng.*, February 1898; *Berg. u. Hütten. Zeit.*, 1898, 57, 117; *J. Soc. Chem. Ind.*, 1898, 17, 582.

<sup>2</sup> Fresenius, *Z. anal. Chem.*, 1870, 9, 127.

and the silver precipitated with hydrochloric acid; the filtrate is evaporated to dryness with sulphuric acid, the residue is taken up with water, lead sulphate filtered off, the copper deposited electrolytically and tested for bismuth, and in the residual solution zinc, nickel, and iron determined by the usual methods (*cf.* Analysis of Bronze, pp. 208 *et seq.*).

#### 8. COPPER LIQUORS

From 10 to 50 c.c. of the liquor, according to the content of copper, are evaporated with an excess of sulphuric acid, any lead sulphate that has separated filtered off, and the copper precipitated in the filtrate by pure zinc. The iron is determined at once in the decanted solution by titration with potassium permanganate.

#### 9. COPPER-PLATING BATHS

Fifty c.c. of the solution are evaporated with an excess of sulphuric acid in a draught place to decompose the cyanogen compounds present, and heated until fumes of sulphuric acid are copiously evolved. The residue is allowed to cool, dissolved in water, and the copper estimated electrolytically. In most cases it suffices to first decompose the cyanogen compounds, and then to titrate the ammoniacal solution with potassium cyanide (*cf.* p. 173).

### LEAD

Until recently, the metal content in ores and in products from lead-smelting works (except in the case of the metal itself and of hard lead) was invariably estimated in metallurgical works by quick, dry methods,<sup>1</sup> although such assays gave results from 1.5 to 5 per cent. too low.

On account of the considerable inaccuracy of dry assaying, rapid volumetric methods have been introduced, and, having proved reliable, are now much used in the laboratories of smelting works, but more especially in commercial laboratories; in the ore market of the United States, for instance, the valuations of lead ores are now based entirely on the results of the "wet assay."

The products to be examined include: Ores, the products from smelting works (lead matte, lead speiss, litharge, scum, dross, lead fume, slags, work lead, refined lead or commercial lead, hard lead or antimonial lead), lead alloys, scrap lead, etc.

The most important ores of lead are:—

*Galena*,  $\text{PbS}$ , containing 86.6 per cent. of lead; it invariably contains silver as isomorphous,  $\text{Ag}_2\text{S}$ , sometimes in quantities over 1 per cent., but most frequently the silver content is from  $\frac{1}{100}$  to  $\frac{1}{10}$  per cent.

<sup>1</sup> Details on "Lead Assaying" are given by J. and J. Beringer, *Text Book of Assaying*, 12th ed., 1910, and by Bruno Kerl, *Probierbuch*, 2nd ed., 1894.



*Cerussite*,  $\text{PbCO}_3$ , containing 77.6 per cent. of lead.

*Anglesite*,  $\text{PbSO}_4$ , containing 68.3 per cent. of lead.

*Pyromorphite*, or *Green Lead Ore*,  $3\text{Pb}_3\text{P}_2\text{O}_8 + \text{PbCl}_2$ , containing 76.2 per cent. of lead.

The following ores are more rare :—

*Mimetisite*,  $3\text{Pb}_3\text{As}_2\text{O}_8 + \text{PbCl}_2$ .

*Crocoisite*,  $\text{PbCrO}_4$ ; *Wulfenite*,  $\text{PbMoO}_4$ .

*Vanadinite*,  $3\text{Pb}_3\text{V}_2\text{O}_8 + \text{PbCl}_2$ ; *Stolzite*,  $\text{PbWO}_4$ .

## I.—DRY ASSAYS FOR ORES, ETC.

Dry assays consist in the separation of the metal by fusion with reducing and fluxing agents; sulphide ores or metallurgical products are (when fused in clay crucibles) desulphurised by addition of metallic iron, or the fusion is carried out in an iron crucible. On account of the volatility of the metal at high temperatures (increased by the presence of arsenic, antimony, and zinc), and to a less extent through scorification, there is always a considerable loss of metal. In the case of impure ores containing antimony, arsenic, copper, zinc, bismuth, etc., the lead is always more or less contaminated by these impurities.

The noble metals are generally determined by special assays (*cf.* Silver). They may, however, also be estimated by a direct cupellation of the crude lead button, obtained by the "assay in an iron crucible" method (*cf.* Cupellation of Silver, pp. 105 *et seq.*).

### 1. The Precipitation or Belgian Assay in an Iron Crucible.

This, the best of all dry assays for lead, is specially suited for rich, pure galenas. It permits of a larger weight of ore being worked upon than the other assays, and is quick, thereby preventing any great loss of lead. Under the most favourable conditions, a pure galena will yield 85.25 per cent. of lead instead of 86.6 per cent.; the average loss of lead by this assay may be taken at about 2 per cent.

To carry out the determination, a stout iron crucible, about 12 cm. high and 8 cm. in diameter at the top, is heated to a red heat in a wind furnace, the ore and fluxes introduced (*e.g.*, 30 g. ore, 30 g. sodium carbonate, and 3 g. argol; 5 to 10 g. of borax or sodium carbonate may be placed behind this mixture on the metal scoop (Fig. 37, p. 103) and will form a cover to the rest of the charge in the crucible), the crucible is covered and brought to a bright red heat in about ten minutes; within another ten minutes the fluxes become placid and fluid. The crucible is then removed from the furnace, allowed to cool for a few minutes, and the thin fluid contents run into a warm mould (Fig. 40, p. 104) smeared with black lead. When cold, the slag and lead button are separated by a few blows of a hammer, the button cleaned by wash-

ing in hot water and brushing with a stiff brush, then dried and weighed.

Immediately after pouring out the first assay, a further 20 g. of flux mixture are fused in the crucible, and, after heating for about ten minutes, the contents are run into the mould, sometimes yielding another small button of lead; a new assay may then be carried out.

These assays are in use in many lead-smelting works; they are specially adapted to the estimation of the content of lead in lead drosses of very varying composition, of which large average samples (after sieving) must be taken.

Any antimony contained in the ore is found nearly quantitatively in the lead button, and may be determined as described under "Hard Lead," p. 235.

W. Witter<sup>1</sup> mixes 25 g. of ore with 30 g. of "flux" (72 parts sodium carbonate, 40 parts borax, 9 parts tartaric acid), adds a covering of 15 g. of flux and a further 15 g. of flux, when molten, so as to carry down any particles of lead which may adhere to the sides of the crucible.

J. Flath<sup>2</sup> obtained the best yield of lead by fusing 25 g. of the sample (galenas of varying richness, galena with pyrites, pyromorphite, cerussite, flue dust, lead slags) with 60 g. of a flux consisting of 70 per cent. calcined sodium carbonate, 28 per cent. calcined borax, and 2 per cent. tartaric acid. The above works equally well with basic or with acidic ores. The greatest difference compared with a wet assay showed a loss of 1.5 per cent. The method cannot be recommended for lead slags (*cf.* p. 241).

For pyromorphite and mixtures containing phosphates, Beringer<sup>3</sup> recommends the following charge:—Ore 20 g., sodium carbonate 25 g., argol 7 g., fluor spar 5 g., 2 g. of borax being used as a cover.

## 2. Other Methods of Assay for Ores containing Sulphur.

Smaller weighings (1 assay hundredweight = 5 g. or 3.75 g.) of ores containing rather large quantities of gangue and small quantities of foreign sulphides are frequently fused in clay assay crucibles with potassium carbonate and flour, borax, and metallic iron (pieces of telegraph wire 15 mm. long), the crucible broken when cold, the lead separated from the excess of iron, cleaned and weighed (German assay).

A very practical American procedure is to place one or more strong iron nails in the crucible during the fusion, which are carefully removed after withdrawing the crucible out of the furnace. The assay takes about one hour. This method is often used in England, hoop iron

<sup>1</sup> Private communication to Prof. Pufahl.

<sup>2</sup> *Chem. Zeit.*, 1900, 24, 263; *J. Chem. Soc. Abstr.*, 1900, 78, 512; *J. Soc. Chem. Ind.*, 1900, 19, 470.

<sup>3</sup> *Text Book of Assaying*, 12th ed., 1910, p. 212.

being employed, and a similar charge to that given for the iron pot method.

The Isleman, or Upper Hartz potassium carbonate assay, consists in fusing the ore mixed only with potassium carbonate and covered with a layer of common salt, in small crucibles, in a muffle furnace; the precise method of procedure depends very much on the character of the ore. It gives very varying results. Any silver in the ore is retained quantitatively in the lead button.

The sulphuric acid assay, which consists in the preparation of lead sulphate, as pure as possible, by wet means, and the fusion of this with sodium carbonate, argol, and iron, is specially suited for very impure ores largely contaminated by foreign metallic sulphides.

### 3. Methods of Assay for Oxidised Ores and Metallurgical Products.

These substances (*e.g.*, cerussite and litharge) are fused with fluxes and reducing agents in clay pots; in presence of sulphur (*e.g.*, anglesite, scum, lead fume), the addition of iron is necessary, and with a high content of "earths" (*e.g.*, marl in "bottoms"), the free addition of borax. Slags and poor wastes are fused in larger quantities in crucibles with reducing solvent agents.

## II.—WET ASSAY FOR ORES, ETC.

The gravimetric methods of Rössler and of Schulz and Low, the electrolytic methods and the volumetric methods of assay, are regarded as quick methods.

### A. GRAVIMETRIC METHODS.

#### 1. Determination of the Lead as Sulphate.

In the case of ores free from antimony (galena with zinc blende, pyrites, arsenical pyrites, copper pyrites, etc., and gangue) 1 g. of the very finely ground ore is treated in an Erlenmeyer flask with 10 c.c. of nitric acid (sp. gr. 1.4), the contents of the flask stirred round and placed in a slanting position on a hot sand-bath. When the oxidation is complete (after about half an hour), 10 c.c. of 50 per cent. sulphuric acid are added, the contents of the flask mixed and boiled on the sand-bath till sulphuric acid fumes are evolved. To the cooled residue 30 c.c. of water are added, the contents of the flask warmed on a boiling water-bath (or on a sand-bath) for fifteen minutes, cooled, the solution containing the iron, copper, zinc, etc., decanted through a filter paper, the impure lead sulphate washed once by decantation with water acidified with sulphuric acid (0.5 c.c. sulphuric acid in 100 c.c. water) and twice with pure water, 20 c.c. of concentrated ammonium acetate solution



(prepared by neutralising ordinary ammonium hydroxide with 50 per cent. acetic acid), a few drops of ammonia and 20 c.c. of water added, and the contents of the flask heated to boiling so as to completely dissolve the lead sulphate. The hot solution is then filtered into a beaker through the paper that was used for the first decantation, the flask and filter paper washed three times with hot water to which some ammonium acetate has been added, and the lead precipitated again as sulphate in the cooled solution (about 200 c.c.) by the addition of 10 c.c. of sulphuric acid.

The heavy precipitate is filtered off after standing for one to two hours, washed three times with pure water (the slight solubility of lead sulphate in water may be neglected in this instance), and once with strong alcohol, the paper and precipitate dried in an air-bath, the sulphate removed as completely as possible on to glazed paper, the filter paper ignited at a low temperature in a weighed porcelain dish, the bulk of the precipitate added, gradually heated to a dull red heat, and weighed.  $\text{PbSO}_4 \times 0.6831 = \text{Pb}$ .

If small globules of lead become reduced on the ignition of the filter paper, a few drops of dilute nitric acid are added, the crucible warmed on the water-bath to dissolve the lead, a drop of sulphuric acid added, evaporated, the sulphuric acid driven off, and then the bulk of dry lead sulphate added.

In the case of ores poor in lead, lead mattes, etc., 5 g. may be taken for the assay.

If the ore contains much chalky gangue, a light precipitate of very fine matted needles of calcium sulphate may form over the heavy lead sulphate on cooling the acetate solution to which sulphuric acid has been added. In such cases the clear solution is decanted as completely as possible from the precipitate, 200 c.c. of water and a few drops of sulphuric acid added, the whole heated for an hour in a boiling water-bath, stirred round frequently, completely cooled, the pure lead sulphate collected on a filter paper and treated as above.

Calcareous ores containing a very small amount of lead are best dissolved in hydrochloric acid, the solution diluted with boiling water (on account of the difficultly soluble lead chloride), filtered into a beaker, the lead, dissolved copper, etc., precipitated by sulphuretted hydrogen, the impure lead sulphide washed off the filter paper, and treated with nitric acid and sulphuric acid as above.

Galena containing antimony is decomposed with strong nitric acid (10 c.c. of sp. gr. 1.4) and 2 g. of tartaric acid in a flask, 50 c.c. of water added, warmed, cooled after ten minutes, and the lead precipitated by the addition of 10 c.c. of sulphuric acid, whereby a small quantity, about 2 mg., remains in solution. After standing for an hour the solution is decanted off, the sulphate washed, dissolved in ammonium acetate

and further treated as above. A. H. Low treats galena containing antimony and bismuth with strong nitric acid, boils with sulphuric acid, takes up with water, decants off the sulphuric acid solution, and dissolves the antimony out of the impure lead sulphate by boiling it with a solution of 2 g. of Rochelle salt (potassium sodium tartrate) in 50 c.c. of water to which 1 c.c. of sulphuric acid is added.

Ores rich in antimony (*e.g.*, Bournonite,  $\text{CuPbSbS}_3$ ) and products from smelting works (lead speisses) are best fused with sodium carbonate and sulphur (or dehydrated sodium thiosulphate), lixiviated with hot water, the insoluble sulphides of lead, copper, iron, etc., collected on a filter paper, washed, transferred from the filter into a dish, treated with nitric acid, and then further with sulphuric acid as above. Antimony and arsenic may be estimated in the solution of the sulpho-salts (p. 284).

In the first filtrate from the lead sulphate (see above) the copper, zinc, iron, etc., may, of course, be determined by first precipitating the copper, together with bismuth, arsenic, antimony, etc., by sulphuretted hydrogen. The washed lead sulphate may be quickly and completely converted into carbonate by boiling with sodium carbonate or by digesting with a cold, saturated solution of ammonium carbonate. If the lead carbonate is washed with hot water, dissolved in dilute nitric acid, the gangue filtered off, and sufficient nitric acid added so that the solution contains fifteen to twenty volumes per cent. of nitric acid of sp. gr. 1.38, a solution is obtained suited to the electrolytic separation of the lead as peroxide (*cf.* p. 226).

## 2. The Determination of the Lead as Metal or as Alloyed with Wood's Metal.

1. *v. Schulz and Low's Method*.<sup>1</sup>—The lead sulphate from 1 g. of ore (see above), purified by boiling with Rochelle salt solution acidified with dilute sulphuric acid, is dissolved off the filter by a boiling, saturated solution of ammonium chloride, after being previously washed with dilute sulphuric acid. The filtrate, after the addition of three small pieces of aluminium foil (1.5 mm. thick, 35 mm. long, and 15 mm. wide), is boiled for five minutes so as to separate the lead as metal. The flask is then filled with cold water, its contents emptied into a large porcelain basin, the lead adhering to the aluminium scraped off under water, the liquid decanted off, and the lead washed into a small porcelain dish. After pouring off the water, the lead is pressed together by means of a small agate pestle, washed several times with distilled water, once with absolute alcohol, then dried quickly in an air-bath, and weighed. The total duration of the assay from the decomposition of the ore is forty minutes.

<sup>1</sup> *Chem. News*, 1893, 67, 178.

2. *C. Rössler's Method*.<sup>1</sup>—The lead is separated in the spongy condition out of as pure a solution as possible of lead chloride (free from copper and antimony) by means of pure granulated zinc, and the washed lead collected under hot water in a weighed quantity of molten Wood's metal. In the case of ores containing copper and antimony, lead sulphate in as pure a condition as possible is prepared (according to the previously mentioned methods), which, in presence of dilute hydrochloric acid is just as quickly reduced by zinc as lead chloride. The Wood's alloy required for the assay is prepared by melting together twenty parts of the purest bismuth, ten parts of lead, five parts of tin, and five parts of cadmium in a small porcelain basin, a small piece of paraffin also being added. If the paraffin begins to burn, the basin is covered with an iron plate. When the fused alloy has cooled somewhat it is well stirred with folded filter paper, and then the molten alloy is immediately poured into an iron mould. The sticks so obtained are broken up by a sharp chisel into pieces weighing about 2 g.

Pure lead-free zinc is used either granulated or as thin foil. The latter is prepared by melting 50 to 100 g. of zinc in a clay or porcelain crucible over a triple Bunsen burner, removing the skin of oxide by introducing a small piece of ammonium chloride, and then pouring the metal, in a thin stream, on to a stone slab or iron plate from a height of 10 to 20 cm.; when cold it is cut up into strips.

To carry out the determination, 0.5 to 1 g. of the very finely ground ore (galena, cerussite, or litharge) is treated in a large test tube (180 mm. long by 30 mm. wide) with 20 to 30 c.c. of ordinary 25 per cent. hydrochloric acid; the tube is then placed in an inclined position on a hot sand-bath and heated until the ore is completely decomposed; 20 to 30 c.c. of water are then added, 1 to 1.5 g. of zinc allowed to slide into the inclined tube, a small thin glass funnel with a short wide tube placed in the mouth of the test tube, which is then placed in a water-bath heated to about 70°. The separation of lead takes place very quickly, and the spongy lead is generally carried to the surface along with the zinc, on account of the occluded hydrogen bubbles. The lead should be made to sink by separating it from the zinc residue by means of a long thin glass rod, and pressing it against the walls of the tube. When the evolution of hydrogen has completely stopped, the solution is tested for lead by introducing about 6 sq. mm. of magnesium ribbon. If the magnesium dissolves without leaving a small bead of lead the separation is complete, otherwise a further addition of a few decigrams of zinc and some hydrochloric acid is made, the tube again heated, and the contents again tested with magnesium. The solution is then heated till the evolution of hydrogen

<sup>1</sup> *Z. anal. Chem.*, 1885, 24, 1; *J. Chem. Soc. Abstr.*, 1885, 48, 596.



has ceased, the acid zinc solution decanted into a beaker, the residue of lead washed by decantation three times with about 30 c.c. of boiled, hot water, hot water again poured on to the spongy lead, a weighed piece of Wood's alloy introduced, the test tube placed for a few minutes in boiling water and well stirred round, thus forming an alloy of Wood's alloy and lead, melting below  $100^{\circ}$ . By cooling in cold water, the alloy is solidified; it is then shaken out, dried, and weighed; the gain in weight is due to the lead from the assay. Water may frequently be enclosed in the alloy, so that Rössler advises heating it on a pitted porcelain plate to  $100^{\circ}$  for a short time in an air-bath before weighing.

This assay is suited for pure galenas (or galenas containing zinc blende) with calcareous gangue which dissolve completely in hydrochloric acid. Any insoluble residues (gangue, pyrites, etc.) find their way into the spongy lead and also to some extent into the alloy. The solution may be separated from these solid residues by filtration, using a small asbestos filter, but then, on account of the sparing solubility of lead chloride, more solution is obtained than is desirable. If copper pyrites is present, the ore is best treated with nitric and sulphuric acids, and the lead sulphate reduced in presence of dilute hydrochloric acid. Any antimony may then be removed, by evaporating the lead solution to dryness and heating the residue to  $250^{\circ}$  so as to volatilise the antimony chloride.

### 3. Electrolytic separation of Lead as Peroxide.<sup>1</sup>

On the introduction of electrolytic methods of analysis, C. Luckow found as early as 1865 that lead is separated quantitatively as hydrated peroxide from solutions containing much free nitric acid. This method permits of a separation of lead from copper, gold, mercury, antimony, zinc, cadmium, iron, nickel, cobalt, manganese, and aluminium; silver and bismuth are partially separated as peroxides together with the lead.

Details of the apparatus employed in electrolytic analysis are given under "Copper," pp. 159 *et seq.*

The solution employed for the electrolysis must be free from chlorine compounds, and should contain but little sulphuric acid, since this is partially deposited with the peroxide of lead. By the use of platinum basins, sand-blasted or "matted" on the inside, up to 4 g. of peroxide may be firmly deposited; with smooth dishes the deposit easily scales off.

For slow deposition at ordinary temperatures, using a low current density (0.05 ampères per 100 sq. cm.), the solution should contain about

<sup>1</sup> Cf. Literature on Electrolytic Analysis, p. 159; also, H. Nissenson and C. Rüst, *Z. anal. Chem.*, 1893, 32, 431; Medicus, *Ber.*, 1892, 25, 2490; *J. Soc. Chem. Ind.*, 1893, 12, 182; *Chem. Zeit.*, 1895, 19, 1143; *J. Soc. Chem. Ind.*, 1895, 14, 1063.

10 per cent. by volume of nitric acid (sp. gr. 1.38), otherwise a separation of metallic lead takes place on the cathode; using a current of  $ND_{100} = 0.5$  ampère, the content of nitric acid should be raised to 20 per cent. by volume.

For more rapid deposition, the method commonly adopted in practical work, a current of 1 to 2 ampères at 2.3 to 2.7 volts is used at ordinary temperatures in a solution containing 20 per cent. by volume of nitric acid (sp. gr. 1.38); at higher temperatures, not above 60° to 70°, 10 per cent. by volume of nitric acid is sufficient. When, on addition of 20 c.c. of water, the freshly wetted surface of the matted dish does not become darkened by further separation of lead peroxide in a quarter or half an hour, the deposition is completed. The current is then switched off, the contents of the dish emptied out, the deposit washed three times with boiling water and once with absolute alcohol, dried in an air-bath at 200° for half an hour, and weighed, after allowing to cool for half an hour. The lead peroxide is quickly dissolved off the platinum dish by means of hot, very dilute nitric acid, with addition of small quantities of oxalic acid.

A micro-burner may be advantageously used for warming the dish (to 50° to 60°), a piece of asbestos paper being placed under the dish so as to distribute the heat evenly. In case any lead peroxide becomes detached on washing the dish, the washings must be carefully decanted. The drying must be done at 200°, otherwise a small amount of water is retained by the deposit. When properly carried out, the method gives very accurate results.

Rotating electrodes may be used to hasten the precipitation of the lead peroxide. F. Exner<sup>1</sup> adds 20 c.c. of concentrated nitric acid to the lead nitrate solution, giving a total volume of 125 c.c., and uses a current of 10 ampères at 4.5 volts, with a rotating cathode which makes 600 revolutions per minute. The deposit has a uniform velvety black colour; the time required for the deposition is from ten to fifteen minutes. R. O. Smith<sup>2</sup> effects the deposition on a rotating spiral which makes 800 revolutions per minute. A nitric acid solution is used, containing 25 c.c. of nitric acid of sp. gr. 1.4 in 125 c.c. of solution, which is electrolysed at 95°, with a current of 10 to 11 ampères per 100 sq. cm. at 3.6 to 3.8 volts; up to 0.58 g. of lead can be precipitated in fifteen minutes.

H. J. S. Sand<sup>3</sup> has studied the behaviour of a lead peroxide anode deposit on drying and the effect of varying conditions on its nature. His results show that too much nitric acid should be avoided, that it is specially important to remove any oxides of nitrogen that may be present by evaporating the solution to be electrolysed to dryness before

<sup>1</sup> *J. Amer. Chem. Soc.*, 1903, 25, 904.

<sup>2</sup> *Ibid.*, 1905, 27, 1287.

<sup>3</sup> *Faraday Soc.*, 1910, p. 207; *J. Soc. Chem. Ind.*, 1910, 29, 47.

a determination, and that the temperature should be kept below  $97^{\circ}$ . The deposited peroxide should be dried in an atmosphere free from moisture, preferably by washing with alcohol and ether in the usual way, and drying over a Bunsen burner, as it is capable of absorbing moisture at about  $200^{\circ}$ .

## B. VOLUMETRIC METHODS

### I. Alexander's Molybdate Method.<sup>1</sup>

This method is based on the precipitation of lead in hot acetate solution by means of ammonium molybdate, forming lead molybdate, which is insoluble in acetic acid. Excess of ammonium molybdate is recognised by the yellow coloration given to a freshly prepared tannin solution, a drop of the titrated solution being added to a drop of the tannin solution on a pitted porcelain plate. The ammonium molybdate solution is prepared by dissolving 9 g. of the commercial salt in water, adding a few drops of ammonium hydroxide, and diluting to 1 litre. For its standardisation, 300 mg. of lead sulphate are dissolved by warming with a sufficient quantity of dilute ammonium acetate solution, acidified with acetic acid, diluted to 250 c.c., heated to boiling, and titrated with the ammonium molybdate solution till all the lead is precipitated as the heavy white molybdate. Drops of the tannin solution (one part in three hundred parts of water) are placed on the pitted porcelain plate, and drops of the solution being titrated are added from time to time until a yellow coloration is produced (300 mg. of  $\text{PbSO}_4$  contain 204.93 mg. of Pb).

The method is carried out at Broken Hill as follows:—One gram of ore is treated in an Erlenmeyer flask with 15 c.c. of strong nitric acid, 10 c.c. of sulphuric acid added, and the solution boiled till sulphuric fumes are copiously evolved. On cooling, the sulphate is warmed with water, cooled, washed by decantation, first with water acidulated with sulphuric acid, finally with pure water, the decantation washings filtered, the filter paper brought into the flask, 25 c.c. of concentrated ammonium acetate solution added, the solution heated, diluted with 100 c.c. of hot water, and boiled till the lead sulphate has completely dissolved. The solution is then diluted to about 250 c.c. with boiling water, and titrated as above. In the case of ores containing over 30 per cent. of lead, 0.5 g. is taken for the determination. The time required is one hour.

The same quantity of ammonium acetate should be used in each assay, and calcium should be absent.

<sup>1</sup> *Eng. and Min. J.*, 1893, 55, 298; *J. Chem. Soc. Abstr.*, 1893, 64, 599.



## 2. Beebe's Potassium Ferrocyanide Method.<sup>1</sup>

A lead acetate solution, acidified with acetic acid, free from alkali salts, is titrated at the ordinary temperature with a 1 per cent. potassium ferrocyanide solution till a drop gives a brown coloration on a porcelain plate with concentrated uranium acetate solution slightly acidified with acetic acid. The ferrocyanide solution is standardised against a lead acetate solution of known strength.

The impure lead sulphate as obtained from the ore, as described above (pp. 222 *et seq.*), is boiled with Rochelle salt solution, acidified with sulphuric acid, as recommended by A. H. Low (p. 224), for the removal of bismuth and antimony. By digesting the washed sulphate with ammonium carbonate, it is converted into lead carbonate, which is well washed with hot water, dissolved in a beaker in hot dilute acetic acid, so as to avoid loss by spitting, and the cooled solution titrated with potassium ferrocyanide.

According to Low, a high content of calcium compounds (up to 30 per cent. of calcium oxide) does not seriously affect the accuracy of the estimation, provided the calcium sulphate is completely converted into the carbonate; otherwise, lead is precipitated as sulphate on dissolving the carbonate in acetic acid.

## 3. The Chromate Method.

C. and J. J. Beringer<sup>2</sup> have modified Diehl's method, in so far as they precipitate a boiling dilute solution of lead sulphate in sodium acetate with as small an excess as possible of potassium chromate, using neutral silver nitrate solution as indicator by spotting; after cooling and diluting to 200 c.c., the excess of potassium chromate is estimated colorimetrically in 50 c.c. of the filtrate from the lead chromate, after addition of acetic acid, by comparison with standard acidified potassium chromate solutions (*cf.* Heine's Colorimetric Copper Assay, p. 180).

### III.—ANALYSIS OF COMMERCIAL LEAD (SOFT LEAD, REFINED LEAD).

*Fresenius'*<sup>3</sup> *Method, with Modifications by Fernandez-Krug and Hampe.*<sup>4</sup>

Refined lead contains 99.96 to 99.99 per cent. of lead and minute quantities of silver, copper, bismuth, cadmium, arsenic, antimony, iron, nickel, cobalt, zinc, and manganese.

Bright turnings (a few from as many ingots as possible) or bright

<sup>1</sup> *Chem. News*, 1896, 73, 18; *Z. anal. Chem.*, 1897, 36, 58.

<sup>2</sup> *Text Book of Assaying*, 12th ed., 1910, p. 214.

<sup>3</sup> *Quantitative Analysis*, 7th ed., vol. ii., p. 370.

<sup>4</sup> Private communication to Prof. Pufahl from Dr Fernandez-Krug and Dr Hampe.

scrapings are warmed for a short time with dilute hydrochloric acid, washed with water, and dried quickly. Two hundred grams are accurately weighed out and dissolved in a 1500 c.c. covered beaker by gently warming with 500 c.c. of nitric acid of sp. gr. 1.2 and 500 c.c. of water. The solution is left to stand for twelve hours.

Purer kinds of soft lead give a perfectly clear solution. Any precipitate of lead antimoniate, etc., arising on solution or on standing is filtered off; its further treatment is described below.

Fernandez-Krug and Hampe treat the clear or filtered solution in a beaker with 62 to 63 c.c. of pure sulphuric acid, and stir well. When cold, the clear solution is syphoned off into a large beaker, 200 c.c. of water, acidified with nitric acid, poured on to the lead sulphate, well stirred with a thick glass rod, allowed to settle, decanted, and this repeated two to three times with 200 c.c. of acidified water, so as to extract the last trace of dissolved foreign metals out of the precipitate.

The combined washings, together with the syphoned solutions ( $1\frac{1}{2}$  to 2 litres), are not evaporated (Fresenius' method) but saturated in a beaker with ammonia, 25 to 50 c.c. of ammonium sulphide added, and the whole warmed on a water-bath for two to three hours. The precipitate, which contains considerable quantities of lead sulphide, as well as the sulphides of the foreign metals, is filtered off, washed into a large porcelain crucible, and dried. Meanwhile, the residue from the solution of the 200 g. of lead (see above) is dissolved off the filter paper in hydrochloric acid, some tartaric acid and water added, sulphuretted hydrogen passed through, the precipitate containing lead and antimony filtered off, washed into the porcelain crucible, again dried, and the contents fused with six times its weight of the usual mixture of equal parts of sodium carbonate and sulphur.

The solution obtained on lixiviating the fused mass with hot water is added to the filtrate from the precipitation with ammonium sulphide, acetic acid added till acid, which precipitates the sulphides of arsenic and antimony, together with much sulphur, and then heated for three to four hours on a boiling water-bath. The precipitate is filtered off, washed with dilute sulphuretted hydrogen water, acidified with a little acetic acid, dried, the free sulphur extracted with carbon bisulphide, the sulphides dissolved in hydrochloric acid and potassium chlorate, and the undissolved sulphur filtered off; a very small filter paper is used for the filtration, and the washing is done with a pipette. The filtrate, after the addition of 0.5 g. of tartaric acid, is neutralised with ammonia, and finally treated with 10 c.c. of strong ammonia (sp. gr. 0.91) and 1 to 2 c.c. of magnesia mixture (no alcohol). After twenty-four hours the magnesium ammonium arsenate is filtered off on to a small paper and washed with dilute ammonia (one volume of sp. gr. 0.91 to two volumes of water). Ammonium sulphide is added to the filtrate and

washings, the solution warmed, the antimony precipitated as sulphide by adding excess of dilute sulphuric acid, the precipitate filtered off on to a small paper, dissolved in warm ammonium sulphide, the solution evaporated in a weighed porcelain crucible, the residue oxidised with strong nitric acid, evaporated, the sulphuric acid driven off, the residue strongly ignited, and weighed as antimony tetroxide.  $\text{Sb}_2\text{O}_4 \times 0.7898 = \text{Sb}$ .

The previously obtained precipitate of magnesium ammonium arsenate is converted into pyroarsenate (*cf.* Arsenic Determination in Commercial Copper, p. 196) and weighed as such.  $\text{Mg}_2\text{As}_2\text{O}_7 \times 0.4829 = \text{As}$ .

The residue from the lixiviation of the melt of the ammonium sulphide precipitate with sodium carbonate and sulphur contains lead, copper, silver, bismuth, cadmium, zinc, iron, nickel, cobalt, and manganese, as sulphides. For their oxidation by heating with dilute nitric acid (one volume acid of sp. gr. 1.2 to two volumes water), the small filter paper is spread out in a porcelain dish, the acid poured on, and then covered with a clock-glass. After filtration and washing, the lead is separated by evaporation with sulphuric acid, and the residue of lead sulphate taken up with a little water and filtered off. A considerable excess of sulphuric acid must be used, otherwise some bismuth may be retained by the lead sulphate; recent analyses show that soft leads containing considerable amounts of bismuth occur in commerce.

The filtrate from the lead sulphate is treated with saturated sulphuretted hydrogen water, sulphuretted hydrogen passed in, and the solution gently warmed for some time; copper, bismuth, silver, and cadmium are precipitated and collected on a small filter paper, the filtrate containing iron, zinc, nickel, etc., being set on one side for the time being.

The precipitate is oxidised as before with dilute nitric acid, the nitric acid driven off by evaporating with a few drops of sulphuric acid, the residue taken up with a little water, nearly neutralised with pure sodium hydroxide (from metal), then sodium carbonate and some pure potassium cyanide added, and the solution gently warmed. A precipitate of bismuth is thus obtained which is filtered off, washed, dissolved in a small quantity of nitric acid, reprecipitated with a slight excess of ammonia, filtered off, dissolved in nitric acid, the solution (now free from sulphuric acid) evaporated in a weighed porcelain crucible, the residue heated to a dull red heat, and weighed as bismuth oxide (*cf.* Bismuth Determination in Commercial Copper, p. 199).  $\text{Bi}_2\text{O}_3 \times 0.8965 = \text{Bi}$ .

The filtrate containing potassium cyanide from the bismuth precipitate is treated with a further quantity of cyanide and then a few drops of potassium sulphide solution. A precipitate of silver sulphide and cadmium sulphide may be formed, which is filtered off and dissolved in hot dilute nitric acid. The silver is precipitated by the addition of a few drops of hydrochloric acid and the silver chloride filtered off.



The filtrate is evaporated to dryness, any cadmium precipitated by boiling with sodium carbonate, the precipitate collected on a small filter paper, washed with hot water, dissolved in a few drops of nitric acid, the solution evaporated in a weighed porcelain crucible, and the residue converted into cadmium oxide by carefully heating to a red heat.  $\text{CdO} \times 0.8754 = \text{Cd}$ . Cadmium is but seldom found in commercial lead, and only in traces.

The filtrate from the silver and cadmium sulphides is evaporated to dryness after the addition of some sulphuric, nitric, and a few drops of hydrochloric acid. The residue is taken up with water, the solution filtered if necessary, the copper precipitated by passing sulphuretted hydrogen, and estimated as sulphide (*cf.* Copper p. 169).  $\text{Cu}_2\text{S} \times 0.7986 = \text{Cu}$ .

The solution containing the zinc, iron, nickel, etc. (see above), is made slightly alkaline in a flat-bottomed flask, ammonium sulphide added, and the contents diluted so as to fill the flask up to the neck, the flask corked and allowed to stand for twenty-four hours or longer. The precipitate is not filtered off until it has completely settled. The filtrate, which may contain some nickel in solution, is acidified with acetic acid, ammonium acetate added, warmed for a few hours, and the sulphur and nickel sulphide filtered off.

The precipitate from the ammonium sulphide is treated immediately after filtration on the filter paper with a solution of six parts of saturated sulphuretted hydrogen water and one part of hydrochloric acid of sp. gr. 1.12, the liquid that runs through being again brought on to the filter paper by means of a pipette. Zinc sulphide and iron sulphide are dissolved, whilst nickel and cobalt sulphides remain on the paper. After drying this small filter, it is ignited, together with that on which the nickel sulphide containing sulphur was collected, in a porcelain crucible, the residue warmed with a few drops of aqua regia, the solution evaporated completely to dryness, a little ammonia and ammonium carbonate solution added, filtered, boiled in a platinum dish with potassium hydroxide till all the ammonia is driven off, the small amount of precipitate collected on a small filter paper, washed, dried, ignited, and weighed as nickel oxide.  $\text{NiO} \times 0.7858 = \text{Ni}$ .

After weighing, the oxide is tested qualitatively for cobalt by the borax bead.

The solution containing zinc, iron, and manganese obtained on treating the ammonium sulphide precipitate with sulphuretted hydrogen water and dilute hydrochloric acid is evaporated, oxidised with a drop of nitric acid, precipitated with ammonia, the precipitate filtered off, redissolved in hydrochloric acid, precipitated again with ammonia, washed, dried, ignited, and the iron oxide obtained weighed.  $\text{Fe}_2\text{O}_3 \times 0.6994 = \text{Fe}$ .

As a check, it can be dissolved by warming with a little hydrochloric acid, the diluted solution warmed to  $70^\circ$  with potassium iodide, cooled,

and the free iodine titrated with sodium thiosulphate in presence of starch solution.

The ammoniacal filtrate from the ferric hydroxide is treated with ammonium sulphide and gently warmed for at least twenty-four hours. Any precipitate that separates is filtered off, washed, and immediately treated on the filter paper with dilute acetic acid so as to dissolve any manganese sulphide mixed with the zinc sulphide. The trace of zinc sulphide is dissolved off the paper in a little hydrochloric acid, the solution evaporated to dryness in a small weighed platinum dish, some moist precipitated mercuric oxide added (which must volatilise without leaving any weighable residue), the whole evaporated to dryness, gradually heated to a bright red heat, and the residue of zinc oxide weighed (Volhard's method).  $\text{ZnO} \times 0.8034 = \text{Zn}$ .

The acetic acid solution is evaporated, any manganese precipitated with potassium hydroxide, the precipitate filtered off, the filter paper washed, dried, ignited, the residue ignited with good access of air and weighed.  $\text{Mn}_3\text{O}_4 \times 0.7203 = \text{Mn}$ .

The silver<sup>1</sup> in refined lead is nearly always determined by cupellation (*cf.* "Silver," p. 105); the content of lead is given by difference.

*Remarks.*—On account of the impurities in soft lead being present in extremely minute quantities, its analysis is most difficult and demands much practical experience. The acids and other reagents used must be carefully tested for impurities, and the filter papers must be free from iron. In spite of all care, on account of the lengthy analysis, dust finds its way into the solutions, which causes the iron content to invariably come out too high.

For the manufacture of white lead, accumulators, etc., only the most exceptionally pure kinds of soft lead are suitable.

#### IV.—ANALYSIS OF HARD LEAD (ANTIMONIAL LEAD)

*Nissenson and Neumann's Method.*<sup>2</sup>—Hard lead is now generally manufactured in metallurgical works with a high content of antimony (up to 28 per cent.); a weighing of 1 to 2.5 g. is sufficient for the estimation of the antimony and impurities (copper, arsenic, and frequently tin).

<sup>1</sup> The silver in soft lead may be accurately determined by wet methods according to Bannow and Krämer (who were the first to recognise the bad effect of silver on lead for the manufacture of white lead, arising from a red coloration due to oxide of silver), by digesting at least 200 g. with insufficient nitric acid for its complete solution (400 c.c. of nitric acid of sp. gr. 1.2 for 200 g. of lead) for a long time, pouring off the solution, dissolving the residue in dilute nitric acid, and precipitating the silver by the addition of an aqueous solution of lead chloride. If the residue does not dissolve completely in nitric acid (lead antimoniate, etc.), the insoluble matter is filtered off, dried, fused with sodium carbonate and sulphur, the melt lixiviated with water, the residue (lead sulphide with a little silver sulphide) dissolved in nitric acid, the solution added to the above solution containing silver, and the silver then precipitated with lead chloride.

<sup>2</sup> *Chem. Zeit.*, 1895, **19**, 1142; *J. Soc. Chem. Ind.*, 1895, **14**, 1063.

Nissenson and Neumann dissolve 2.5 g. of metal in a 250 c.c. flask by warming with a mixture of 4 c.c. of nitric acid (sp. gr. 1.4), 15 c.c. of water and 10 g. of tartaric acid; after cooling, 4 c.c. of concentrated sulphuric acid are added, the solution diluted, cooled, and made up to the mark; the lead is thus completely precipitated as sulphate. The solution is filtered through a dry paper, 50 c.c. of the filtrate (corresponding to 0.5 g. of metal) made strongly alkaline with sodium hydroxide, 50 c.c. of a cold saturated solution of pure sodium sulphide added, the solution boiled, filtered, the residue washed, and the solution, heated to about  $80^{\circ}$  (and kept at this temperature in the dish by means of a micro-burner), electrolysed in a matted dish for an hour with a current of 2 ampères and an E.M.F. of 2 to 3 volts. Up to 0.2 per cent. of any arsenic present may (according to W. Witter) be deposited with the antimony; tin is not deposited.

The dish is washed with water without interrupting the current, the apparatus then taken apart, the dish washed a few times with hot water and once finally with absolute alcohol, then dried at  $90^{\circ}$ , either in an air-bath or on a boiling water-bath, and weighed, after allowing to cool for thirty minutes. The antimony, which is especially adherent to the inside of the matted dish (p. 162), is dissolved off by a mixture of dilute nitric and tartaric acids.

For the estimation of the copper, the precipitate (copper sulphide) formed on warming with sodium sulphide is dissolved in nitric acid, the solution filtered, and the copper determined electrolytically; or if only a small amount be present, it may be estimated colorimetrically.

If the hard lead contains tin, the solution from which the antimony has been deposited, together with the washings, are evaporated to 150 c.c., 25 g. of ammonium sulphate added, the solution boiled and then electrolysed for one hour at a temperature of from  $50^{\circ}$  to  $60^{\circ}$ , with a current of 1 to 2 ampères at 3 to 4 volts. The dish is washed without breaking the circuit, any sulphur which has separated on the surface of the tin removed mechanically, the dish rinsed out with water, dried, and weighed.

Since the amount of tin is usually very small, it may be precipitated as sulphide in the solution from the deposition of the antimony by acidifying with dilute sulphuric acid. The precipitate is filtered off, dried, and, by very careful heating and final strong ignition with addition of ammonium carbonate in a porcelain crucible, converted into stannic oxide, which is weighed.

If the hard lead contains tin and arsenic, these are best separated by F. W. Clarke's<sup>1</sup> method.

<sup>1</sup> Cf. Fresenius, *Quantitative Analysis*, 7th ed., vol. i., p. 490. On the precipitation of antimony by sulphuretted hydrogen in the presence of oxalic acid, see:—F. W. Clarke, *Chem. News*, 1870, **21**, 124; Lesser, *Z. anal. Chem.*, 1888, **27**, 218; Warren, *Chem. News*, 1890, **62**, 216; J. Clark, *J. Chem. Soc.*, 1892, **61**, 424; Henz, *Z. anorg. Chem.*, 1903, **37**, 1.

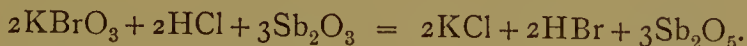


W. Witter<sup>1</sup> effects the separation as follows:—Fifty c.c. of the filtrate from the lead sulphate (see above), corresponding to 0.5 g. of metal, are made alkaline with ammonia, just acidified with hydrochloric acid, 30 g. of oxalic acid added, and sulphuretted hydrogen passed through the boiling solution for twenty minutes. Antimony, arsenic, and copper are precipitated, the small amount of tin remaining in solution. The hot solution is filtered, made slightly ammoniacal, sufficient ammonium sulphide added to redissolve the precipitate at first formed, saturated with acetic acid, the precipitate (tin sulphide and sulphur) allowed to settle, filtered off, and converted into oxide as above.

The arsenic is extracted from the antimony-arsenic precipitate with ammonium carbonate solution, reprecipitated by acidifying with hydrochloric acid, and finally weighed as magnesium pyroarsenate (*cf.* Arsenic, p. 272). The antimony sulphide is then dissolved in 50 c.c. of a cold saturated solution of sodium sulphide, in which 1 g. of sodium hydroxide is dissolved, the solution heated, and the antimony deposited electrolytically in a platinum dish. (The separation of arsenic and antimony by precipitating the arsenic with sulphuretted hydrogen in strong hydrochloric acid solution may be more accurate.)

The small amount of copper sulphide remaining on the filter paper is dissolved in nitric acid, excess of ammonia added, and the copper estimated by titrating with potassium cyanide (*cf.* p. 173).

For the volumetric determination of the antimony in hard lead, H. Nissenson and P. Siedler<sup>2</sup> recommend their modification of S. Györy's<sup>3</sup> method, in which the antimony is titrated with potassium bromate. This solution is made up by dissolving 2.7852 g. of recrystallised potassium bromate, dried at 100°, and diluting to 1 litre; 1 c.c. corresponds exactly to 6 mg. of antimony, according to the equation:—



The method, as further slightly modified by H. W. Rowell,<sup>4</sup> is carried out as follows:—About 1 g. of the metal, as finely subdivided as possible, is gently warmed in a flask with 20 c.c. of brom-hydrochloric acid (saturated solution of bromine in fuming hydrochloric acid), the contents being frequently shaken and warmed till completely decomposed or dissolved. When solution is completed, it is boiled until the vapours appear but slightly yellow in colour. After cooling somewhat, small pieces of sodium sulphite, about 3 or 4 g., are added in two to three portions with shaking, the solution boiled for about five minutes to

<sup>1</sup> Private communication to Prof. Pufahl.

<sup>2</sup> *Chem. Zeit.*, 1903, 27, 749; *J. Soc. Chem. Ind.*, 1903, 22, 967.

<sup>3</sup> *Z. anal. Chem.*, 1893, 32, 415; *J. Chem. Soc. Abstr.*, 1893, 64, 554.

<sup>4</sup> *J. Soc. Chem. Ind.*, 1906, 25, 1181.

drive off the sulphur dioxide, again boiled after the addition of 20 c.c. of strong hydrochloric acid and 40 c.c. of hot water, and the hot solution titrated with the potassium bromate solution. If much arsenic (4 to 5 per cent.) be present, it is necessary to boil down after the addition of the sulphite, take up with 20 c.c. of hydrochloric acid and a crystal of sodium sulphite, and then continue as above. A few drops of methyl orange are added as indicator, and when the red colour disappears, the titration is finished.

The results are very good and not influenced by the copper (0.5 per cent. at most) and small quantity of iron which are present in hard lead.

**Analysis of Hard Lead by the determination of the Specific Gravity.**—The method recommended by G. Faunce,<sup>1</sup> which was not at first adopted on account of the inaccuracies in manipulation, has recently been investigated, and made practicable, by F. W. Küster, P. Siedler, and A. Thiel;<sup>2</sup> they obtained excellent results when the alloys under consideration were solidified without formation of blow holes. On testing a hard lead, prepared by melting together 24 g. of pure lead and 6 g. of pure antimony in an atmosphere of hydrogen, the mean of sixteen determinations gave a specific gravity of 9.977, and the greatest difference from the actual antimony content worked out at 0.08 per cent. The calculation is based on the fact that hard lead containing 20 per cent. of antimony has a specific gravity of 9.977 (Faunce gives 9.974), and that in this alloy the specific gravity varies by 0.060 if the antimony content varies by 1 per cent. (according to Faunce).

In English works the following table is often used to give approximately the amount of antimony contained in antimonial lead:—

Spec. grav.	Per cent. Sb.	Spec. grav.	Per cent. Sb.
11.40	Nil	10.65	10.0
11.35	0.64	10.60	10.7
11.30	1.27	10.55	11.4
11.25	1.90	10.50	12.1
11.20	2.5	10.45	12.8
11.15	3.1	10.40	13.6
11.10	3.8	10.35	14.4
11.05	4.4	10.30	15.2
11.00	5.1	10.25	16.0
10.95	5.8	10.20	16.8
10.90	6.5	10.15	17.6
10.85	7.2	10.10	18.4
10.80	7.9	10.05	19.2
10.75	8.6	10.00	20.0
10.70	9.3		

Silver in hard lead is always determined in the dry way (*cf.* Silver, p. 110) by scorification and cupellation.

<sup>1</sup> *J. anal. Chem.*, 1887, **I**, 123.

<sup>2</sup> *Chem. Zeit.*, 1902, **26**, 1107.

The analysis of hard lead without the use of the electrolytic method of estimation is described by Fresenius.<sup>1</sup>

#### V.—ANALYSIS OF WORK LEAD (*cf.* also, pp. 110 and 128)

The work lead as obtained directly from the ores contains 96 to 99 per cent. of lead, and is either refined, desilverised, and worked up into soft lead at the smelting works, or sent to special refining works. Since the content of impurities is much higher than in soft lead, a much smaller weighing suffices for the analysis, which may be carried out in exactly the same way as a soft lead analysis (*cf.* pp. 229 *et seq.*).

On account of the higher content of antimony, it is best dissolved in a mixture of nitric and tartaric acids.

H. Nissenson and B. Neumann<sup>2</sup> dissolve, according to the purity of the sample, 10 to 50 g.; for 10 g., 16 c.c. of nitric acid (sp. gr. 1.4), 60 c.c. of water, and 5 to 10 g. of tartaric acid is sufficient. The amount of tartaric acid given is sufficient to bring all the antimony in 50 g. into solution. The lead is precipitated out of this solution by the addition of sulphuric acid, 3 c.c. being added for every 10 g. of metal taken, and the solution filtered free from lead.

If the precipitation is done in a graduated flask, which is filled to the mark after cooling, and only a measured quantity of the solution as filtered through a dry paper taken for analysis, the volume of the lead sulphate (2.15 c.c. per 10 g. of lead) must be subtracted, in the manner given by Fresenius<sup>3</sup> for the analysis of soft lead.

The filtrate from the lead sulphate is evaporated and treated with sodium hydroxide and sodium sulphide as in the analysis of hard lead according to Nissenson and Neumann (p. 234). Arsenic, antimony, and tin are dissolved, separated, and determined as described. The residue contains copper, silver, bismuth, cadmium, zinc, iron, cobalt, and nickel, and is further treated as in the case of the analysis of soft lead. Silver is determined in a separate weighing by cupellation (*cf.* pp. 105 *et seq.*).

Nissenson and Neumann recommend the following method for the estimation of only the antimony and copper: the antimony is determined electrolytically (as in the case of hard lead), and the residue from the treatment with sodium sulphide dissolved in aqua regia, saturated with ammonia, filtered, and the copper estimated colorimetrically in a portion of the ammoniacal solution (p. 179).

The sulphur in work lead is determined by heating a fairly large weighing in a current of chlorine, collecting the sulphur chloride in a

<sup>1</sup> *Quantitative Analysis*, 7th ed., vol. ii., p. 375.

<sup>2</sup> *Chem. Zeit.*, 1895, **19**, 1142. *J. Soc. Chem. Ind.*, 1895, **14**, 1063.

<sup>3</sup> *Quantitative Analysis*, 7th ed., vol. ii., p. 373.



receiver and precipitating the sulphuric acid formed from the chloride by barium chloride.

#### VI.—LEAD MATTE, COPPER LEAD MATTE, AND LITHARGE

The silver in these mixtures of sulphur compounds of iron, lead, copper, etc., is always determined by dry methods or by a combined wet and dry method (*cf.* pp. 109 and 222). Lead and copper may be determined by the method given for copper pyrites containing lead (p. 183). The lead sulphate is dissolved in ammonium acetate, the solution either precipitated with sulphuric acid or titrated with ammonium molybdate, or the sulphate converted into carbonate, which is dissolved in nitric acid and electrolysed, etc. (*cf.* Wet Methods of Assaying Lead Ores, p. 222). The copper may be determined either electrolytically or volumetrically (*cf.* Copper Assays for Ores, p. 183).

Nissenson and Neumann (*loc. cit.*) dissolve 1 g. of matte in 30 c.c. of nitric acid (sp. gr. 1.4); the solution is boiled, diluted, filtered, and the lead deposited electrolytically as peroxide in a matted platinum dish. Any copper separated on the cathode soon dissolves in the strong nitric acid solution freed from lead. The solution is evaporated with excess of sulphuric acid, the residue taken up with water, the copper precipitated in the boiling solution by sodium thiosulphate, and finally estimated as copper oxide.

**Litharge** is analysed either by dry methods (*cf.* Lead Assays for oxidised Ores, etc., p. 222) or is fused with sodium carbonate and sulphur, the melt lixiviated, arsenic and antimony estimated in the solution, and lead, bismuth, copper, and iron estimated in the residue by the methods given for the analysis of soft lead (pp. 229 *et seq.*). The amount of copper, which is generally small, may also be determined colorimetrically (p. 179). The silver in the litharge is estimated by the cupellation of the lead button obtained by the lead assay.

#### VII.—RICH LEAD ALLOYS<sup>1</sup>

**Tin-Lead Alloys Rich in Lead.**—One gram of the very finely divided alloy (rolled or scraped) is completely decomposed by warming in a covered porcelain or platinum dish with 20 c.c. of nitric acid of sp. gr. 1.2. One hundred c.c. of boiling water are then added, boiled for five minutes, and the tin oxide filtered off (*cf.* Bronze analysis, p. 208). In the filtrate the lead is estimated by evaporation with sulphuric acid, etc. Since the oxide of tin generally contains small quantities of lead, it is fused after weighing, with sodium carbonate and sulphur, and any lead sulphide remaining after lixiviation with water

<sup>1</sup> For the analysis of Hard Lead, *cf.* pp. 233 *et seq.*

converted into sulphate, which is weighed as such, and the corresponding amount of lead oxide deducted from the weight of impure stannic oxide (*cf.* also, pp. 212 *et seq.*).

Antimony is often present in these alloys, and special precautions are then necessary.

**Type-metal** (Lead, Antimony, Tin).—If it contains only a few per cent. of tin, type metal is analysed like hard lead and dissolved in dilute nitric and tartaric acids (*cf.* p. 234). If it contains a higher content of tin, it is treated like anti-friction or white metal (*cf.* Tin, p. 258).

For determining the lead in alloys of lead, tin, and antimony, Parry<sup>1</sup> recommends the separation of the lead in alkaline solutions; the sulphide is then dissolved in hydrochloric acid with the addition of potassium chlorate, neutralised with ammonia, followed by acetic acid, and titrated with potassium chromate.

**Shot.**—Shot contains from 0.2 to 0.8 per cent. of arsenic in addition to the lead. One gram of the shot, flattened by striking with a hammer, is dissolved in an Erlenmeyer flask by warming on the sand-bath with 20 c.c. of dilute nitric acid (sp. gr. 1.2). Ten c.c. of distilled sulphuric acid are added, and the solution boiled till sulphuric acid fumes are evolved. The cold residue is taken up with water, the lead sulphate filtered off, the filtrate boiled with 20 c.c. of sulphurous acid solution till no smell is recognisable, so as to reduce the arsenic, which is then precipitated by passing in sulphuretted hydrogen, and finally weighed as magnesium pyroarsenate.

In most cases the arsenic is best determined by distillation at 120° with a solution containing 600 g. of calcium chloride, 300 g. of ferric chloride, and 600 c.c. of hydrochloric acid in 1 litre. The solution is boiled gently in the presence of antimony (*cf.* Estimation of Arsenic in Copper, p. 196) for twenty minutes, the distillate collected in a U-tube containing a little water, neutralised with ammonia, just acidified with hydrochloric acid, sodium bicarbonate added, and then titrated with iodine. In the presence of a small quantity of sulphur a little solid mercuric chloride is put into the distillation flask to prevent sulphuretted hydrogen coming over and reprecipitating the arsenic in the U-tube.

Fernandez-Krug and Hampe employ the following method for the analysis of hard lead, type-metal, shot, etc.: 1 g. of the filings or clippings of the alloy are dissolved in a tall beaker in the cold or, at most, at a gentle heat in 12 c.c. of aqua regia (prepared from one volume of nitric acid of sp. gr. 1.4 and three volumes of hydrochloric acid of sp. gr. 1.12). The separated lead chloride is filtered through as small a paper as possible and washed, first with 25 per cent. hydro-

<sup>1</sup> *Analysis of Ashes and Alloys*, 1908, p. 40.

chloric acid and then with absolute alcohol, and weighed as usual.  $\text{PbCl}_2 \times 0.7449 = \text{Pb}$ . The filtrate, diluted to 500 c.c., is saturated with sulphuretted hydrogen, the precipitate allowed to settle for twelve hours, filtered through an asbestos filter, washed with water containing hydrochloric acid and sulphuretted hydrogen, and dried at  $100^\circ$ . The filtrate is again saturated with sulphuretted hydrogen, and may serve for the estimation of the iron, nickel, zinc, and manganese. The dried precipitate, along with the asbestos filter, is placed in a porcelain boat and gently warmed in a current of pure dry chlorine in a piece of combustion tubing (*cf.* pp. 258 *et seq.*, 3. Tin Alloys). The chlorides of arsenic, antimony, tin, and finally bismuth, volatilise and are collected in a three-bulb U-tube containing 50 c.c. of strong hydrochloric acid (consisting of one volume of fuming acid and one volume of acid of sp. gr. 1.12); lead and copper chlorides remain behind and may easily be separated from one another by absolute alcohol. The hydrochloric acid solution containing the volatile chlorides is treated with 5 g. of pure ferrous sulphate, so as to render the arsenic easily precipitable by means of sulphuretted hydrogen, and then saturated with sulphuretted hydrogen in a flask, closed by a rubber stopper, through a hole in which passes the tube through which the sulphuretted hydrogen is led in. The arsenic is completely precipitated in twelve hours, filtered through an asbestos filter, washed with strong hydrochloric acid, and further treated in the usual manner (*cf.* Arsenic, p. 271). The sulphuretted hydrogen is removed from the filtrate by a current of carbon dioxide, and finally with a little brom-hydrochloric acid, the greater part of the acid carefully neutralised with ammonia, and the antimony then precipitated by a few grams of chemically pure (electrolytic) iron. The precipitation is carried out in a 250 c.c. round-bottomed flask, on to which a tubulure, and at an angle of  $120^\circ$  to that a filter tube, closed with an asbestos filter, are blown. During the reduction, carbon dioxide, which can escape through the asbestos filter, is passed into the flask through the tubulure; when the separation of the antimony and solution of the iron are completed, the filter tube is brought into a perpendicular position, and the liquid and washings forced through the filter by means of carbon dioxide. Oxidation of the antimony during filtration and washing is thereby completely prevented. If it is desired to weigh the antimony as such, it is washed finally with absolute alcohol and dried at  $100^\circ$  with the asbestos filter (previously dried and weighed). It is better to dissolve the antimony in hydrochloric acid with the addition of a little potassium chlorate, and, after reduction of this solution with sulphurous acid, to titrate with potassium bromate solution (*cf.* p. 235, Volumetric Determination of Antimony in Hard Lead). The determination of the tin in the filtrate



is effected by precipitation with sulphuretted hydrogen, filtering off the brown precipitate of tin sulphide, and weighing as oxide (*cf.* Tin; 3. Tin Alloys, p. 260). Bismuth may be accurately separated from arsenic and antimony by means of alkaline sulphides.

### VIII.—WASTE LEAD AND LEAD ASHES

*Dry Method.*—A large average sample of several kilograms weight is hammered, the proportion by weight of the flattened metal to the fines determined, each weighed out in this proportion so as to give a total weighing of 50 g., and in this the metal reduced by fusion with sodium carbonate and charcoal, borax, and a covering of common salt in an iron crucible (*cf.* p. 220). The impurities may be determined in the button of lead according to the methods given for the analysis of work lead and hard lead.

*Wet Method.*—Ten grams in all of a mixture of the metallic and the oxidised earthy portions are weighed, dissolved in 75 c.c. of nitric acid of sp. gr. 1.2 with the addition of a few grams of tartaric acid, the solution filtered after dilution with water, cooled, diluted to 500 c.c., 50 c.c. (corresponding to 1 g.) taken, the lead precipitated as sulphate by the addition of 5 c.c. of sulphuric acid, and weighed as such. The impurities (antimony, copper, etc.) may be estimated in the filtrate by the usual methods.

Lead ashes, which frequently contain lead sulphate, are treated with nitric acid, the residue washed, boiled with neutral ammonium acetate, the filtrate diluted to 500 c.c., in 50 c.c. of which (corresponding to 1 g. of substance) the lead is precipitated with sulphuric acid.

### IX.—LEAD SLAGS

For the determination of lead in slags containing much lead, the dry assay gives sufficiently accurate results, but for slags containing only little lead the volumetric method is preferable. From 2 to 5 g. of the finely powdered slag are dissolved in aqua regia, evaporated to dryness to dehydrate the silica, taken up with dilute hydrochloric acid, diluted and filtered. The filtrate is nearly neutralised, and sulphuretted hydrogen passed in to precipitate the lead as sulphide. The precipitate is filtered off, washed, dissolved in nitric acid, and the solution evaporated with sulphuric acid to separate the lead as sulphate; this precipitate is then washed, dissolved in ammonium acetate, and titrated with ammonium molybdate (*cf.* p. 228).

F. S. Schimeska<sup>1</sup> has modified this method in order to adapt it to the rapid determination of lead in slags. In this case 2 g. of the

<sup>1</sup> *Eng. and Min. J.*, 1910, 89, 467.

slag are weighed into a 250 c.c. flask, 15 c.c. of water added, the whole boiled, and then 5 c.c. of concentrated hydrochloric acid added whilst agitating the flask. Immediately solution is complete, 140 c.c. of cold water are added, followed by 50 c.c. of saturated sulphuretted hydrogen water; the flask is then stoppered and vigorously shaken for fifteen seconds. The lead and copper present, which are precipitated in flakes of sulphide, are then filtered off. The occasional precipitation of zinc is of no consequence, and if small particles of slag remain undissolved, they will be attacked in the subsequent treatment. The addition of water to the hydrochloric acid solution of the slag is made quickly, so as to prevent the formation of gelatinous silica. The proportions of acid and water given above must be used, otherwise the lead will not be precipitated. The sulphide precipitate is filtered on to an asbestos filter on the pump, washed twice with water, transferred to a porcelain dish, 2 c.c. of concentrated nitric acid and 8 c.c. of concentrated sulphuric acid added, and the whole boiled until nitrous fumes cease to be evolved. After cooling, 40 c.c. of water are added, the liquid boiled and then filtered on paper or on an asbestos filter; any copper will be found in the filtrate. The filter and precipitate are boiled with ammonium acetate solution, and the solution containing the lead titrated with ammonium molybdate solution.

### X.—LEAD GLAZES

The Home Office gives the following method<sup>1</sup> for the estimation of the soluble lead in lead glazes:—A weighed quantity of the finely ground and dried material is shaken continuously for one hour with one thousand times its weight of 0.25 per cent. hydrochloric acid, and filtered after standing for one hour. The lead is precipitated as sulphide in an aliquot part of the filtrate, and then weighed as sulphate.

### BISMUTH

Bismuth is produced partly directly from ores and partly from intermediate products arising in the working up of work lead containing bismuth (litharge, furnace bottoms, and cupels containing bismuth).

Of the numerous minerals containing bismuth, the following ores are of practical importance:—

*Native Bismuth*, often containing some arsenic.

*Bismuthite*,  $\text{Bi}_2\text{S}_3$ , with 81.2 per cent. Bi.

*Emplecite*,  $\text{CuBiS}_2$ , containing 62.0 per cent. Bi and 18.9 per cent. Cu.

*Bismuth Ochre*,  $\text{Bi}_2\text{O}_3$ , with 89.6 per cent. Bi, containing always some  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{Fe}_2\text{O}_3$ , and, less frequently,  $\text{As}_2\text{O}_5$  also.

<sup>1</sup> Cf. Vol. I., p. 599.

The ores, metallurgical products containing bismuth, and the bismuth alloys are always analysed by wet methods; the dry assays<sup>1</sup> for ores, etc., are, on account of the greater volatility of bismuth, less accurate than the corresponding lead assays, and an impure metal always results, since lead, copper, antimony, arsenic, iron, etc., are easily retained by the bismuth. Only the noble metals in the ores, etc., are determined by dry assays (*cf.* Silver).

## I.—ANALYTICAL METHODS FOR ORES AND METALLURGICAL PRODUCTS

### Fresenius' Method.<sup>2</sup>

This method is suited to all ores, and takes into consideration the presence of bismuth, lead, copper, silver, gold, antimony, arsenic, tin, iron, cobalt, nickel, zinc, sulphur, and tellurium.

For the determination of the bismuth, 2 to 5 g. of the very finely ground ore, dried at 100°, are dissolved in nitric acid of sp. gr. 1.3 (30 to 75 c.c.) with the addition of 2 to 5 g. of tartaric acid, in a flask placed in a slanting position on a sand-bath. The solution, somewhat diluted, is filtered, the filtrate diluted to 100 or 250 c.c., and sulphuretted hydrogen passed in to saturation in the cold. The precipitate is filtered off, washed with sulphuretted hydrogen water, and boiled with sodium sulphide solution. The insoluble sulphides are collected on a filter paper, washed, dissolved by warming with dilute nitric acid, and the solution filtered (from sulphur and any lead sulphate). Sodium carbonate is added to the nitric acid solution (of bismuth, lead, copper, silver) until a permanent precipitate is formed, and then a few grams of pure potassium cyanide. After digesting at a gentle heat for some time (about one hour), the bismuth and lead carbonate precipitate, which retains alkali, is filtered off.

For the separation of the bismuth from the lead, the carbonates are dissolved in hot, dilute nitric acid, the solution evaporated with a good excess of sulphuric acid (about 4 c.c. for a weighing of 1 g.), the residue taken up with a liberal supply of dilute sulphuric acid and well boiled, the lead sulphate, free from bismuth, filtered off and washed with 10 per cent. sulphuric acid. The acid bismuth sulphate solution is diluted, a slight excess of ammonia added, gently warmed, the bismuth hydroxide filtered off and washed for a short time. The impure hydroxide, contaminated with some basic sulphate, is dissolved in a little nitric acid, the pure hydroxide precipitated as above with a slight excess of ammonia, and, after drying, converted into oxide by ignition.

$$\text{Bi}_2\text{O}_3 \times 0.8965 = \text{Bi.}$$

<sup>1</sup> *Cf.* Beringer, *Text Book of Assaying*, 1910, p. 221; Kerl, *Probierbuch*, 2nd ed., p. 145.

<sup>2</sup> Fresenius, *Quantitative Analysis*, 7th ed., vol. ii., p. 418.



If the amount of bismuth is small (up to 0.1 g.), the washed hydroxide is dissolved off the filter paper by dropping hot, dilute nitric acid on to it from a pipette. The solution is evaporated on the water-bath in a weighed porcelain crucible, the crucible then heated on a sand-bath, and the nitrate finally completely decomposed by ignition over a free flame.

Larger quantities of the hydroxide are dried, separated as completely as possible from the filter paper, the portion that remains attached dissolved off as above, the solution evaporated, and then the dried bismuth hydroxide added, etc.

The separation by means of sulphuric acid is satisfactory, provided plenty of acid be used, and the residue be not treated with too much water. Fernandez-Krug and Hampe give the following method for the detection of any retained basic bismuth sulphate:—The washed lead sulphate is washed off the filter paper, the water removed by evaporation, and the sulphate converted into chloride by warming with concentrated hydrochloric acid. After cooling, about 50 c.c. of absolute alcohol are added to the small volume (about 5 c.c.) of hydrochloric acid solution (H. Rose's method), the solution stirred, and after standing for a short time, the alcoholic solution containing all the bismuth (present in the lead sulphate) as chloride is filtered. On diluting with a large volume of water, the bismuth is precipitated as oxychloride, and thus separated from any trace of lead chloride which may have gone into solution.

H. Rose's<sup>1</sup> method of separation, depending on the insolubility of lead chloride in strong alcohol, is less convenient to carry out than the foregoing separation by means of sulphuric acid. The dilute bismuth and lead nitrate solution, corresponding to a weighing of about 1 g., is evaporated to quite a small volume (3 c.c.), rather more strong hydrochloric acid than is necessary for the formation of the chlorides (5 c.c.) added, and stirred for a few minutes at a very gentle heat. After cooling, 25 c.c. of absolute alcohol are added, the solution stirred, the lead chloride filtered off after some time, and washed, first with absolute alcohol and a few drops of hydrochloric acid, and finally with absolute alcohol. By diluting the filtrate from the lead chloride with a quantity of water (500 c.c.), all the bismuth is precipitated as oxychloride, which, after standing for twenty-four hours, is filtered on to a tared, dried filter paper, dried at 110°, and weighed as bismuth oxychloride.  $\text{BiOCl} \times 0.8015 = \text{Bi}$ .

It is quicker to drive off the greater part of the alcohol in the bismuth solution by gently warming, and then precipitate the bismuth hydroxide by a slight excess of ammonia, and weigh as oxide as above.

The estimation of the remaining constituents in bismuth ores is

<sup>1</sup> Rose-Finkener, *Quantitative Analyse*, p. 165.

fully described by Fresenius (*loc. cit.*). The noble metals are always determined by dry assays (*cf.* Silver and Gold).

The analytical methods, which appear somewhat complicated, may in many cases be much simplified, according to the composition of the ores. If, for instance, bismuthite, containing only copper pyrites ( $\text{CuFeS}_2$ ) as impurity, is in question, the first precipitate, with sulphuretted hydrogen ( $\text{Bi}_2\text{S}_3 + x\text{CuS}$ ), naturally need not be extracted with sodium sulphide solution; the copper sulphide is preferably removed by potassium cyanide solution, the residue of bismuth sulphide dissolved in hot, dilute nitric acid, a slight excess of ammonia added, and the precipitated hydroxide converted into bismuth oxide and weighed as such.

Bismuth ochre, if it only contains iron and gangue as impurities, is still simpler to analyse. The filtered diluted nitrate solution is saturated with sulphuretted hydrogen and the bismuth sulphide treated as given for "bismuthite." Bismuth ochre containing arsenic is best dissolved in hydrochloric acid, the gangue filtered off, and the bismuth and arsenic precipitated in the somewhat diluted solution, by sulphuretted hydrogen, etc. (Bismuth arsenate dissolves readily in hydrochloric acid and in hot, strong nitric acid; it is insoluble in cold, dilute nitric acid.) The precipitation of the bismuth as oxychloride by dilution of the hydrochloric acid solution is less reliable.

### W. Heintorf's Methods.<sup>1</sup>

(*For Metallurgical Products containing Bismuth with Lead and Silver.*)

In these methods, which are much recommended, a nitric acid solution is prepared, from which the lead is precipitated by sulphuric acid, and the silver at the same time by sodium chloride. The bismuth in the evaporated, concentrated filtrate is precipitated by ammonium carbonate and ammonia, the precipitate washed with hot water, dissolved in dilute hydrochloric acid, and the bismuth precipitated out of the solution as metal by means of metallic iron. The metal is washed by decantation with hot water, collected on a weighed filter paper, washed once with alcohol, dried for some hours in an air-bath, and the paper and bismuth then weighed between watch-glasses.

(a) **Refined Litharge.**—Two hundred and fifty to five hundred grams of material are fused with potassium carbonate and flour, etc. (*cf.* Dry Lead Assays, p. 222), in five to ten assays (of 50 g. substance), and the metal so reduced further scorified in a muffle furnace till the weight is reduced to two-fifths of the original weighing. The lead thus enriched in bismuth is flattened out, dissolved in hot, dilute nitric acid, and the lead and silver precipitated from the solution. The bismuth in the filtrate

<sup>1</sup> *Berg. u. Hütten. Zeit.*, 1894, 53, 351; *Mineral Industry*, 1894, 3, 425.

from the lead sulphate and silver chloride is washed eight times with water, acidified with sulphuric acid, precipitated as carbonate, dissolved in dilute hydrochloric acid, and the bismuth then precipitated by warming the solution with two or three pieces of iron wire 4 cm. long. The precipitation is known to be completed when a bright piece of iron wire dipped into the solution shows no deposition of bismuth. The acid liquid is poured off, the iron and bismuth washed into a porcelain dish, the bismuth detached from the iron by the fingers, and then the iron removed. After decanting several times with hot water and pouring the decanted washings through a weighed filter paper on account of fine particles of bismuth floating on the surface, the whole of the bismuth is washed on to the paper, washed once with absolute alcohol, dried, and weighed.

(b) **Litharge poor in Bismuth.**—Twenty-five grams are dissolved in nitric acid and treated as given under (a).

(c) **Furnace Bottoms.**—Five grams are fused with "white flux," borax, and glass in a crucible, and the work lead obtained flattened, dissolved, etc., as given under (a).

(d) **Crude Silver.**—Fifty grams are dissolved in nitric acid, the silver precipitated with sodium chloride, the lead with a little sulphuric acid, filtered, washed with water, acidified with sulphuric acid, and the bismuth precipitated in the filtrate as carbonate, etc., as given under (a).

(e) **Ores (Lead Ores poor in Bismuth).**—Five grams are fused in the same manner as furnace bottoms poor in bismuth, but with the addition of 1 g. of assay lead free from bismuth. The flattened button of work lead is dissolved, etc., as above.

### Hampe's Methods for the Determination of Bismuth in Slags from the Refining of Silver.<sup>1</sup>

*(Obtained on fusion of Crude Silver with Quartz Sand and Silver Sulphate.)*

One gram of the finely ground and dried slag is digested in a platinum dish with about 15 c.c. of nitric acid for a long time, and then 10 c.c. of concentrated hydrofluoric acid are added. If the slag is dissolved, a few drops of concentrated sulphuric acid are added, and the contents of the dish are evaporated to dryness. The residue is again dissolved in nitric acid and any graphite (from the crucible) filtered off. After neutralising the filtrate with ammonia, bismuth, lead, and iron, as well as the small quantities of alumina and calcium, are precipitated with ammonium carbonate, the solution boiled, and the precipitate filtered off. The precipitate is dissolved in nitric acid and sulphuretted hydrogen passed into the solution. The precipitated lead and bismuth

<sup>1</sup> *Chem. Zeit.*, 1891, 15, 410; *J. Chem. Soc. Abstr.*, 1892, 62, 919.



sulphides need not be treated with sodium sulphide, since antimony is only present in traces, but are at once dissolved in nitric acid. The solution, filtered free from sulphur, is precipitated with ammonium carbonate, taking the usual precautions, the precipitate containing all the lead and bismuth filtered off, dissolved in hydrochloric acid, and the solution of lead and bismuth chlorides evaporated to complete dryness. The lead chloride is then dissolved by much hot water, whilst the bismuth is precipitated as oxychloride and filtered off. The bismuth oxychloride is dissolved in nitric acid, precipitated with ammonium carbonate, filtered, and the filter paper with the precipitate dried. When dry, as much of the bismuth carbonate as possible is removed from the paper and set on one side. Any carbonate remaining attached to the filter paper is dissolved off in nitric acid, the solution evaporated to dryness in a weighed porcelain crucible, the greater part of the precipitate then added and carefully ignited, after which the bismuth oxide is weighed.

### The Colorimetric Determination of Small Quantities of Bismuth.<sup>1</sup>

This method depends upon the fact pointed out by Stone,<sup>2</sup> that an excess of potassium iodide, added to a dilute sulphuric acid solution of bismuth, produces a yellow colour the intensity of which is directly proportional to the amount of bismuth present. As it is not necessary to obtain the bismuth as a pure salt, practically all the sources of trouble in separation are absent. The object is to first obtain a solution free from large quantities of lead, copper, tin, antimony, gold, and silver, then to precipitate the bismuth as oxychloride, together with possible traces of these metals, arsenic, or tellurium, and to apply the colorimetric method to the solution of this precipitate in sulphuric acid. *Ores, mattes*, etc., are dissolved in hydrochloric and nitric acids, the silica removed as usual, and the filtrates treated as described under copper or lead, with the exception that hydrochloric acid must be removed by evaporating with sulphuric acid to precipitate any lead. Samples containing large amounts of tin, antimony, or arsenic may be fused with a mixture of equal parts of sodium carbonate and sulphur, and the melt dissolved in water and boiled, when all the bismuth is found in the black residue on filtering, and may be dissolved in nitric acid. Ten grams of *copper* are dissolved in 60 c.c. of nitric acid (1:1), the solution diluted with 150 c.c. of water, and a saturated solution of sodium carbonate added till a slight permanent precipitate forms; 1 c.c. is added in excess, which brings down all the bismuth and some copper, and the whole is boiled for five minutes and allowed to settle. The precipitate is filtered off, washed once, and dissolved through the paper back into the original beaker with hydrochloric acid, and

<sup>1</sup> Rowell, *J. Soc. Chem. Ind.*, 1908, 27, 102,

<sup>2</sup> *Ibid.*, 1887, 6, 416.

the bismuth precipitated as basic chloride and, if necessary, re-precipitated to separate the remaining copper as directed below. Ten grams of *refined lead, base bullion*, etc., are dissolved in 80 c.c. of water and 20 c.c. of nitric acid (sp. gr. 1.42), boiled to precipitate most of the tin and antimony, and a small excess of sodium chloride solution (1 : 200) added to precipitate the silver. The lead is precipitated by adding 60 c.c. of boiling sulphuric acid (1 : 20), drop by drop, to the boiling solution, with constant stirring, and then 30 c.c. of sulphuric acid (1 : 3) in excess. The liquid is cooled and allowed to stand an hour, filtered, and the precipitate washed several times by decantation with sulphuric acid (1 : 20). Five c.c. of strong hydrochloric acid are added to the filtrate, and a slight excess of ammonia, then a few drops of hydrochloric acid (1 : 5), till a drop of methyl orange in the solution indicates that it is just acid, when it is boiled for a minute and allowed to stand in a warm place for an hour. The precipitate is collected on a filter and washed twice, and the acidity of the filtrate readjusted to see if it is free from bismuth, or it is tested with potassium iodide. The filter and precipitate are now pulped with 10 c.c. of sulphuric acid (1 : 3), 30 c.c. of water added, and the solution boiled, cooled thoroughly to separate any lead sulphate, and filtered through a Hirsch's or similar funnel on the filter pump, and the paper pulp carefully washed with sulphuric acid (1 : 20). All, or a suitable fraction of the filtrate, containing possibly antimony, arsenic, tellurium, iron, and traces of lead, copper, or silver, and not more than 2 or 3 mg. of bismuth, is placed in one of a pair of 10-inch Nessler tubes, and 5 c.c. of sulphuric acid (1 : 3) with some water in the other, and both are shaken up after the addition of 5 c.c. of potassium iodide (20 per cent.) and ten drops of sulphurous acid (one part saturated solution to two parts water). The blank tube is titrated with a standard solution of bismuth (made by dissolving 0.1 g. of pure metal in 10 c.c. of strong nitric acid and making up to 1000 c.c. with water), till the colour of about 120 c.c. matches that of an equal volume of the test solution.

Arsenic, antimonie, and nitrous acids and ferric salts, or excessive quantities of sulphuric or nitric acids, sulphates, or nitrates throw out iodine, which is removed by prolonged boiling, or more easily by sulphurous acid. A hot solution of bismuth iodide is a little darker than when cold, and in the presence of tellurium, boiling, permanently and slightly darkens the colour. A large excess of sulphurous acid produces an iodine colour, which is removed by the addition of more potassium iodide. Alkalis in excess, ammonium acetate, hydrochloric acid, and chlorides bleach the colour, but the addition of more sulphuric acid or potassium iodide restores it. Experiments show that any precipitates of copper or silver iodides or metallic tellurium may be filtered off without losing any bismuth, but that lead iodide carries a

large proportion of the bismuth with it. Two milligrams of lead, copper, or silver may be present in the Nessler tube without giving a precipitate or darkening the colour, but a careful watch must be kept on this, as a very slight precipitate considerably darkens the tint.

Two operators using the apparatus shown below, clearly and correctly distinguished between the following quantities of bismuth, which were unknown to them, and also between various other intermediate quantities in 125 c.c. of solution:—None and 0.00001 g., 0.00020 g. and 0.000225 g., 0.0010 g. and 0.00105 g., 0.0020 g. and 0.0021 g., 0.0030 g. and 0.0031 g.; 0.00001 g. represents one part in twelve and a half millions, and these figures show that this colour test is at least twice as delicate as Nessler's test for ammonia, and that the limit of error is within 5 per cent. of the bismuth present, which means that a result of 0.001 per cent. is correct to within 0.00005 per cent., or a result of 0.10 per cent. is within 0.005 per cent. of the truth.

The apparatus is a simple form of colorimeter (Figs. 64 and 65), where all light is cut off except the small amount diffused through the ground glass at the bottom of the front side, and reflected through the length of the tubes to the eye by the slip of ground white glass. The light metal shade is made to fit one or both eyes closely, at the discretion of the operator, and can be removed to manipulate the tubes. A thin metal partition separates the tubes, all is painted dead black, and the light which enters is diffused to prevent reflection on the polished sides of the tubes as much as possible. The apparatus is applicable to the colorimetric determination of copper, iron, ammonia, and titanium as well as of bismuth.



FIG. 64.



FIG. 65.

- A.—Metal shade.
- B.—Glass tubes to contain liquids for comparison.
- C.—White ground glass reflector.
- D.—Transparent ground glass.

## II.—COMMERCIAL BISMUTH

For some years bismuth has been put on the market in a very pure condition, since it is chiefly manufactured for pharmaceutical preparations and must comply with the requirements of the Pharmacopœia (as regards its freedom from arsenic, etc.). Smaller quantities of bismuth are used for the preparation of fusible alloys (bismuth with tin, lead, and also cadmium), which, *e.g.*, find application in safety appliances for steam boilers.



Crude bismuth is frequently largely contaminated by antimony, arsenic, copper, lead, and sulphur.

**Qualitative Detection of the Impurities.**—Two grams of the metal are dissolved by warming in 30 c.c. of nitric acid (sp. gr. 1.2); if a permanent milkiness is produced of antimony or tin (bismuth arsenate dissolves), 30 c.c. of water are added, the solution boiled for a few minutes, and the precipitate, to be investigated later, filtered off. Any silver in the filtrate is precipitated as chloride by a few drops of hydrochloric acid, and the filtrate from the silver chloride evaporated to quite a small volume (3 to 5 c.c.). Ten cubic centimetres of fuming hydrochloric acid are then added, well stirred, 30 c.c. of absolute alcohol added, again well stirred, allowed to stand a quarter of an hour, and the separated lead chloride filtered off. The filtrate is evaporated on the water-bath to 10 c.c., 150 c.c. of boiling water added, the bismuth oxychloride filtered off, the filtrate from which is concentrated by evaporation to about 20 c.c., and one-half of the solution saturated with ammonia: iron is precipitated as brown flocculent hydroxide; copper gives a blue solution. A fair quantity of the oxychloride precipitate is dissolved in the other half of the filtrate from the bismuth oxychloride by addition of hydrochloric acid, and the solution tested for arsenic in a simple Marsh apparatus. Arsenic may also be recognised by the blowpipe; alloyed with an equal weight of zinc, bismuth containing arsenic evolves hydrogen containing arseniuretted hydrogen in a Marsh apparatus.

**Quantitative Analysis.**—On solidifying, that part of the metal which solidifies last is very rich in impurities, and is squeezed out of the bar or cake and solidifies on the surface in the form of a protuberance. In sampling, this protuberance is removed by a chisel, its weight and the ratio of its weight to that of the total weight of the ingot determined, and then (after pulverising the protuberance) proportional quantities of the impure protuberance and of the purer, remaining part of the ingot mixed for the sample.

Three grams of the sample are dissolved in 50 c.c. of nitric acid (sp. gr. 1.2) and 3 g. of tartaric acid in a flask over a free flame, the nitrous fumes boiled off, the solution cooled, brought into a beaker, diluted to 200 to 300 c.c., and sulphuretted hydrogen passed in for a long time without warming. After several hours the sulphides are filtered off, washed with sulphuretted hydrogen water, and the filtrate again saturated with sulphuretted hydrogen, and gently warmed for twenty-four hours. By this treatment a further small quantity of arsenic sulphide may separate, which is filtered off, dissolved off the filter paper by a saturated solution of ammonium carbonate and again reprecipitated by adding excess of hydrochloric acid, and warming. In the filtrate from the sulphuretted hydrogen precipitates,

the iron is precipitated by saturating with ammonia, adding ammonium sulphide, and warming. The iron sulphide is filtered off, dissolved in hydrochloric acid, the solution evaporated, oxidised with bromine water, and then precipitated as hydroxide by ammonia, and either weighed as ferric oxide or titrated.

The sulphides are digested for several hours with yellow sodium sulphide solution. A trace of bismuth may be dissolved. It will be found with the arsenic and other sulphides, and is removed together with traces of copper, by treating the ammoniacal solution (to which some tartaric acid is added) carefully with sulphuretted hydrogen water according to Finkener's method. The solution containing the antimony, arsenic, and possibly tin, is filtered, the sulphides reprecipitated in the filtrate by acidifying with dilute sulphuric acid, and warming for a good time on a boiling water-bath. They are then filtered off, washed with hot water to which some ammonium acetate and acetic acid is added, finally once with pure water, then with absolute alcohol. In order to remove as much as possible of the sulphur from the precipitate, the filter tube is corked up, carbon bisulphide poured on to the paper, and allowed to stand for several hours. After running off the carbon bisulphide, and after the residue left on the paper has evaporated, the sulphides are dissolved off the filter paper in warm dilute hydrochloric acid to which some potassium chlorate is added. To the solution strong hydrochloric acid is added, and the arsenic precipitated as sulphide by saturating with sulphuretted hydrogen for a long time. The sulphide is filtered off on to an asbestos filter, and dissolved in hydrochloric acid and potassium chlorate; to this solution the solution of the small amount of arsenic previously precipitated (see above) is added, and then concentrated by evaporation. The concentrated solution thus obtained is saturated with ammonia, magnesia mixture and alcohol added, and the ammonium magnesium arsenate so obtained ignited, and finally weighed as magnesium pyroarsenate (*cf.* Arsenic, p. 272).

To the strongly acid filtrate from the arsenic sulphide some tartaric acid is added, the solution much diluted, antimony and tin precipitated as sulphides by passing in sulphuretted hydrogen, and separated and determined as described on p. 260. Tin is only very seldom found in commercial bismuth.

The sulphides insoluble in sodium sulphide solution are first washed with dilute sulphuretted hydrogen water, then washed into a dish with a very little water, a few grams of solid potassium cyanide added, gently warmed for half an hour, the solution containing all the copper and silver filtered, and the residue washed first with potassium cyanide solution and then with dilute sulphuretted hydrogen water. The solution containing the copper and silver is acidified with nitric acid, warmed until all the separated cuprous cyanide is redissolved, and the

silver cyanide filtered off. The filtrate is evaporated with sulphuric acid until the hydrocyanic acid is completely driven off, the residue dissolved in a little water, and the small amount of copper precipitated by sulphuretted hydrogen water. The copper sulphide is filtered off and estimated as cupric oxide. After drying, the silver cyanide is placed together with the filter paper in a weighed porcelain crucible, strongly ignited with good access of air, and the metallic silver weighed.

The bismuth sulphide, still mixed with some lead sulphide, is dissolved in dilute nitric acid, the somewhat diluted filtrate filtered free from sulphur, and evaporated first in a porcelain dish, and finally in a beaker to a very small volume (about 5 c.c.). To the cold, syrupy liquid, fuming hydrochloric acid is added (according to H. Rose's method<sup>1</sup>) in such quantity that a portion of the clear solution does not become immediately turbid on the addition of a few drops of water; for 2 g. of bismuth 7 c.c. of pure fuming hydrochloric acid suffice. A few drops of dilute sulphuric acid are then added, and the solution allowed to stand for some time, with frequent stirring, so as to convert the lead chloride, which separates at first, into sulphate. Thirty c.c. of alcohol (sp. gr. 0.8) are then added to the contents of the beaker, which are well stirred, and the settled lead sulphate filtered off after a few hours. It is washed first with alcohol to which a few drops of hydrochloric acid are added, then with water, dried, etc. (*cf.* "Lead," p. 222), and finally weighed as lead sulphate. The alcoholic bismuth chloride solution is diluted with 500 c.c. of water and the bismuth precipitated as oxychloride, which is contaminated with some basic sulphate. It is filtered off, dissolved in dilute nitric acid, the solution neutralised with ammonia, ammonium carbonate added, boiled, the bismuth carbonate filtered off, washed with hot water, and finally weighed as oxide (*cf.* Hampe's method of estimating bismuth, etc., p. 246).

If it be desired to separate the lead, which, if present, is generally in very small quantity, from the bismuth by means of sulphuric acid, a large quantity of sulphuric acid must be added to the nitrate solution of the two sulphides, and the solution evaporated, etc., otherwise insoluble basic bismuth sulphate is readily formed.

*Selenium* and *Tellurium* are found in Bolivian and other kinds of foreign bismuth. For their estimation, 10 to 20 g. of the metal are dissolved in a slight excess of nitric acid, the cold solution diluted with double the volume of water (no basic nitrate should separate), sulphur dioxide passed in for several hours, and after standing for two and a half hours, the precipitate containing silver, selenium, and tellurium filtered off, and treated further as described for the estimation of selenium and tellurium in commercial copper, p. 202.

<sup>1</sup> Rose-Finkener, *Quantitative Analyse*, vol. ii., p. 164.



*Sulphur* is determined (in crude bismuth) by dissolving 10 g. in aqua regia, diluting, warming, and adding hot, dilute barium chloride solution. After standing for twenty-four hours the cleared solution is poured off, the precipitate of barium sulphate and silver chloride brought on to a double filter paper, washed with dilute hydrochloric acid, then with water, finally with ammonia, and weighed as barium sulphate.

*The Noble Metals* (silver and sometimes a trace of gold) are best determined by the cupellation of 50 g. of metal in a correspondingly large cupel (*cf.* Silver). E. A. Smith<sup>1</sup> has estimated the noble metals in different kinds of bismuth, and found, *e.g.*, in an assay of Australian bismuth, 0.011 per cent. of gold and 0.3319 per cent. of silver.

### The Electrolytic Determination of Bismuth.

According to O. Brunck's<sup>2</sup> modification of K. Wimmenauer's method, the electrolytic determination of bismuth is carried out as follows:—A nitrate solution, free from chloride, is prepared containing not more than 2 per cent. of acid. A maximum E.M.F. of 2 volts is used. With solutions containing more than 1 per cent. of metal, a current density of 0.5 ampère per 100 sq. cm. and over may be employed; with weaker solutions it is well not to use more than 0.1 ampère. At the commencement of the electrolysis the solution is heated to 70° or 80°, and allowed to cool down of itself whilst the electrolysis proceeds. The deposition on a Winkler gauze cathode is complete in from two to three hours. The deposited metal is of a light reddish grey colour, dense and adhesive. The washing must be done without breaking the circuit, otherwise appreciable quantities of bismuth are redissolved. The results are very accurate.

The rapid precipitation of bismuth with the use of a rotating anode and mercury cathode is described by E. F. Smith.<sup>3</sup>

### III.—ANALYSIS OF BISMUTH ALLOYS<sup>4</sup>

Only the fusible alloys need be considered, the composition of which is given below. The analysis of Wood's metal (bismuth, lead, tin, and cadmium) will serve as an example.

One gram of the metal, as finely divided as possible, is completely decomposed by warming on the water-bath in a covered porcelain dish with 15 c.c. of nitric acid, the solution evaporated to dryness, the residue taken up by warming with very dilute nitric acid, the tin oxide con-

<sup>1</sup> *J. Soc. Chem. Ind.*, 1893, **12**, 316.

<sup>2</sup> *Ber.*, 1902, **35**, 1871; *Z. angew. Chem.*, 1902, **15**, 735; *J. Chem. Soc. Abstr.*, 1902, **82**, 478.

<sup>3</sup> *Electro-Analysis*, p. 99.

<sup>4</sup> *Cf.* Fresenius, *Quantitative Analysis*, 7th edition, vol. ii., p. 420; also, Jannasch and Etz, *Ber.*, 25, 736 (Bromine Method); *J. Chem. Soc. Abstr.*, 1892, **62**, 385, 540, 754.

taminated with lead oxide and bismuth oxide filtered off, washed with boiling water, ignited, and weighed. In order to estimate the impurities, the weighed, impure tin oxide is fused with six times its weight of sodium carbonate and sulphur (or dehydrated sodium thiosulphate), the melt lixiviated with hot water, and the sulphides of lead and bismuth estimated in the residue by H. Rose's method, as described on p. 252. The lead is estimated as sulphate and the bismuth as oxide, and the weight of the two oxides subtracted from the weight of the impure tin oxide.

The filtrate from the stannic oxide is evaporated to dryness, and the nitrates of bismuth, lead, and cadmium converted into the chlorides by twice evaporating on the water-bath with about 20 c.c. of hydrochloric acid. The lead is separated as chloride by H. Rose's method (p. 244), and collected on a weighed filter paper. The alcoholic solution of bismuth and cadmium chlorides is very largely diluted and the precipitate of pure bismuth oxychloride formed, filtered off on to a weighed paper, and weighed after drying for several hours at 100°. The cadmium chloride solution (filtrate from bismuth oxychloride) is evaporated in a dish with a slight excess of sulphuric acid to quite a small volume, the solution removed to a weighed porcelain or platinum crucible, again evaporated, the slight excess of sulphuric acid driven off, the residue ignited moderately strongly, and finally weighed as cadmium sulphate. The cadmium may also be precipitated in the filtrate from the bismuth oxychloride by sulphuretted hydrogen, the cadmium sulphide dissolved in hot dilute nitric acid, and the solution evaporated with a slight excess of sulphuric acid, etc., as above.  $\text{PbCl}_2 \times 0.7449 = \text{Pb}$ ;  $\text{CdSO}_4 \times 0.5392 = \text{Cd}$ .

The best known fusible alloys are:<sup>1</sup>—

	Composition.				Melting-point.
	Bi.	Pb.	Sn.	Cd.	°C.
Newton's . . .	2	5	3	...	94.5
Rose's . . .	2	1	1	...	93.75
Lichtenberg's . . .	5	3	2	...	91.6
Wood's . . .	4	2	1	1	71.0
Lipowitz's . . .	15	8	4	3	60.0

## TIN

The following ores and products occur for examination:—Cassiterite (tin-stone), tin pyrites, the commercial metal, tin alloys, tinplate waste, tin ashes and residues, and tin slags.

<sup>1</sup> From *Handbook of Metallurgy*, Schnabel and Louis, 1908, 2nd edition, vol. ii., p. 448.

The tin content in pure ores is sometimes determined by the dry methods; all other materials are submitted to analysis. The noble metals in tin-stone are determined by scorifying with a large quantity of assay lead (thirty times the weight), and cupelling the work lead obtained after the concentration or by pot assay (*cf.* pp. 99 and 128).

*Tin Ore.*—Tin-stone,  $\text{SnO}_2$ , which contains 78.7 per cent. of tin, is the only ore of importance; it is accompanied by gangue, frequently by wolframite, arsenical pyrites, molybdenite and pyrites, and less frequently by galena and zinc blende. In the secondary formation, as stream-tin, it frequently occurs along with other specifically heavy minerals, such as wolframite, titaniferous iron ore, columbite, spinelle, granite, etc., and also frequently contains some gold.

*Tin Pyrites*,  $\text{Cu}_2\text{FeSnS}_4$ , which contains 24 to 31 per cent. of tin and 24 to 30 per cent. of copper, is only seldom found (Cornwall, Peru), and then not in large quantities.

### I.—ASSAY OF TIN-STONE<sup>1</sup>

Well-prepared, rich ores may be reduced to metal with good results; poor ores are first freed from the greater part of the gangue by washing, which is easily carried out owing to the high specific gravity of cassiterite (6.8). To obtain as pure a metal as possible out of the assay, the metallic impurities (iron, tungsten, etc.) are separated beforehand as far as possible. In many cases this "washing" assay is the only one required, the result being returned as "black-tin."

The fusion of the ore with reducing and fluxing agents is carried out in fire-clay crucibles in a wind furnace. According to the very exhaustive investigations of H. O. Hofman, Mitchell's potassium cyanide assay<sup>2</sup> gives the best results, although a carbon reduction method is largely used in Cornwall.

*Purification of the Sample of Ore.*—Ten grams of the finely ground average sample are spread on a roasting dish and heated in a muffle, and the calcined material brought into a porcelain dish or basin, in which it is boiled with 30 c.c. of aqua regia. By this means most of the iron is dissolved and the wolframite decomposed. After ten minutes the acid solution is carefully poured off, and the residue boiled with 30 c.c. of hydrochloric acid; if only a little further quantity of iron is dissolved, the acid is allowed to remain, otherwise it is boiled up with a fresh quantity of acid, after decanting. After

<sup>1</sup> *Cf.* Kerl, *Probierebuch*, 2nd edition; also, "The Dry Assaying of Tin Ores," by H. O. Hofman, *Berg. u. Hütten. Zeit.*, 1890, 49, 342, 350, 357; *J. Soc. Chem. Ind.*, 1890, 9, 899, 1154; H. Rennie and W. Derrick, *J. Soc. Chem. Ind.*, 1892, 11, 662; J. Gray, *J. Chem. Met. and Min. Soc. of S. Africa*, 1910, 10, 312.

<sup>2</sup> *Manual of Assaying*, 1881, p. 481.



washing twice with water by decantation, the tungstic acid, which is nearly always present, is dissolved in slightly warmed ammonia, and the purified ore dried after again washing with water.

*The Assay by Fusion with Potassium Cyanide.*—About 5 g. of potassium cyanide (98 per cent.) broken up into coarse lumps is placed in the bottom of a clay crucible 12 to 15 cm. high, the ore, intimately mixed with 20 g. of potassium cyanide, then introduced, a covering of 5 g. of potassium cyanide added on the top, and the crucible placed in a moderately hot fire. The fire is kept as hot as possible during the short duration of the assay (fifteen to twenty-five minutes) without allowing the potassium cyanide to boil. The crucible is then removed from the fire, its contents poured into a warmed mould (Fig. 40, p. 104), the slag washed away by water, and the button of metal weighed. Any other small beads of tin found are added.

With a prepared tin-stone from Dakota, which on analysis gave 67.84 per cent. of tin, Hofman obtained a result only 0.35 per cent. low, as a mean of three assays by means of potassium cyanide, which agreed completely between themselves. The German method of conducting the potassium cyanide assay, consisting in a previous ignition of the ore mixed with charcoal, etc., gave very unsatisfactory results, up to 3.73 per cent. low.

The button obtained is naturally not absolutely pure; it always contains small quantities of iron, etc. Any gold in the ore goes completely into the button of tin, as was shown by Pufahl<sup>1</sup> in a tin-stone (stream-tin) from Victoria, rich in gold; by dissolving the flattened or rolled tin in hydrochloric acid the gold remains undissolved as a brown powder.

*Other Methods.*—A very good method for practically all tin ores consists in reducing the purified ore, by strongly igniting in a porcelain tube, in a current of hydrogen or coal gas, dissolving the reduced metal in hydrochloric acid, and determining the tin gravimetrically or volumetrically.<sup>2</sup>

Föhr<sup>3</sup> roasts the ore, boils it with hydrochloric acid, filters, boils the residue again with hydrofluoric acid, ignites it finally with ammonium fluoride, and so obtains pure black tin, which is calculated to tin.

Analytical methods for tin-stone and tin pyrites are described by Fresenius.<sup>4</sup> Tin-stone may be assayed by fusion with sodium carbonate and sulphur (H. Rose's method); tin pyrites is dissolved in aqua regia, etc.

<sup>1</sup> *Berg. u. Hütten. Zeit.*, 1886, 45, 174. Cf. Bannister, *Trans. Inst. Min. and Met.*, 1905-6, p. 513.

<sup>2</sup> Cf. *Text Book of Assaying*, C. and J. J. Beringer, 12th edition, 1910, p. 285.

<sup>3</sup> *Chem. Technol. Zeit.*, 1887, p. 452.

*Quantitative Analysis*, 7th edition, vol. ii., pp. 427-428.

The Pearce-Low<sup>1</sup> method, which is largely used for tin ores and slags, consists in fusing the finely ground material with about ten times its weight of sodium hydroxide<sup>2</sup> in an iron crucible, pouring the molten mass into a clean nickel crucible, from which it is quite easily detached, taking up with water, acidifying with hydrochloric acid, reducing by means of iron or nickel, and titrating in the cold with iodine (*cf.* p. 268).

J. Darroch and C. Meiklejohn<sup>3</sup> use the following method for all tin ores, slags, etc.:—Half a gram of material is fused in a nickel crucible with 3 to 10 g. of sodium peroxide. The fused mass is taken up with boiling water, acidified with hydrochloric acid, and the tin precipitated on zinc. The tin and excess of zinc are dissolved in hydrochloric acid, the solution boiled and titrated with ferric chloride solution. If interfering elements are present, the acidified solution is boiled with iron, and the precipitate filtered off previous to the separation of the tin by means of zinc.

A method specially suitable for ores containing tungsten, and recommended by Donath and Müllner<sup>4</sup> for the separation of tin oxide from tungstic acid, consists in mixing the material with zinc dust or zinc filings and strongly igniting in a covered porcelain crucible for fifteen minutes. The product is treated with dilute hydrochloric acid and boiled until evolution of hydrogen ceases, and then treated with potassium chlorate until the blue tungstic oxide is oxidised to tungstic acid. Water is added to the solution, which is filtered after twenty-four hours; the solution contains the tin.

## II.—ANALYSIS OF COMMERCIAL TIN, ALLOYS, ETC.

### i. Analysis of Tin.

*Estimation of Arsenic.*—Ten grams of the metal, in small pieces, are dissolved in 50 c.c. of ordinary hydrochloric acid with the addition of a little potassium chlorate, the solution cooled, one-third of its volume of fuming hydrochloric acid added, and sulphuretted hydrogen passed in for a long time. The arsenic sulphide is filtered off on to an asbestos filter, and washed first with hydrochloric acid, then with boiled water. It is dissolved in ammonia, the solution evaporated in a porcelain dish, the residue dissolved in strong nitric acid, and the arsenic precipitated in a beaker by magnesia mixture, ammonia, and alcohol as ammonium-magnesium arsenate. This is weighed either as pyroarsenate or converted into silver arsenate (*cf.* Arsenic, pp. 272 *et seq.*).

<sup>1</sup> A. H. Low, *Technical Methods of Ore Analysis*, 1908, 3rd edition, pp. 208-213.

<sup>2</sup> *Cf.* C. A. Burghardt, *Chem. News*, 1890, 61, 260; E. S. Simpson, *ibid.*, 1909, 99, 243.

<sup>3</sup> *Eng. and Min. J.*, 1906, 81, 1177.

<sup>4</sup> *Monatsh.*, 1888, 8, 647; *J. Chem. Soc. Abstr.*, 1888, 54, 531. *Cf.* also T. Moore, *Chem. News*, 1893, 67, 267.

*Estimation of Lead, Copper, and Iron.*—Ten grams of the metal are dissolved in the smallest possible quantity of hydrochloric acid with the addition of potassium chlorate; when solution is complete, the liquid should be of a distinctly yellow colour. Thirty grams of tartaric acid (specially tested for lead) are then added as ammonium tartrate, the solution cooled, saturated with ammonia, sulphuretted hydrogen water added, drop by drop, till no more precipitate is formed, and after gently warming on the water-bath, the sulphides of copper, lead, and iron filtered off. The sulphides, after washing with very dilute sulphuretted hydrogen water, slightly acidified with sulphuric acid, are dissolved in hot nitric acid, the solution transferred to a porcelain dish, the filter ash added, evaporated on the water-bath with a slight excess of sulphuric acid, the residue heated on a sand-bath till fumes of sulphuric acid commence to be evolved, allowed to cool, the residue taken up with a little water, and the lead sulphate, which usually contains a trace of tin, filtered off. After weighing the impure lead sulphate, it is extracted by warming with a solution of ammonium acetate, the lead again precipitated by sulphuretted hydrogen and converted into pure lead sulphate. In the acid filtrate from the impure lead sulphate, the copper is precipitated by sulphuretted hydrogen, and in the filtrate from the copper the iron is finally precipitated by oxidation with bromine water, and warming with excess of ammonia.

Commercial tin fairly frequently contains antimony, and is then analysed like white-metal (No. 3).

## 2. Tin in Tinplate Residues

is determined by the methods either of Lunge and Marmier or Mastbaum, described under "Iron" (pp. 79-80).

## 3. Tin Alloys.

White-metals (antifriction metals), britannia metal, and similar alloys of tin with antimony, lead, copper, iron, sometimes also containing mercury and zinc.

(a) *White-metals containing a high percentage of Tin.*—The best white-metals, containing a high percentage of tin, are conveniently decomposed by treatment with chlorine. Finkener weighs out about 1 g. of the alloy into a porcelain boat, which is then placed in a combustion tube about 70 cm. long, which is bent at right angles at one end, and drawn out for 20 cm. from the bend. The end of the drawn-out tube dips deeply into a three-bulb U-tube containing dilute hydrochloric acid (1 : 3) and some tartaric acid, which is joined up with a similar U-tube containing dilute sodium hydroxide (1 : 1). The end of the tube and receiver are connected by means of a bored cork (not rubber), and the tube itself is somewhat finely drawn out at the end,



so that the condensed volatile chlorides may drop into the receiver. The chlorine is generated from the best pyrolusite in small lumps and strong hydrochloric acid in a 2 litre flask, which is gently warmed on a water-bath. The chlorine is washed first with water and then dried by passing through one or two wash-bottles containing concentrated sulphuric acid. The chlorine is not allowed to enter the combustion tube and react with the alloy in the boat until all the air has been driven out of the generator and wash-bottles. When no further reaction is noticeable at the ordinary temperature, the centre of the tube, the part containing the boat, is gently warmed by means of a Bunsen burner. Finally, the heat is increased till the contents of the boat melt, and then, by progressive heating of the tube in the direction of the receiver, the easily volatile chlorides of tin, bismuth, mercury, and arsenic are driven over into the receiver. The excess of chlorine is absorbed in the second receiver. When the action of the chlorine is ended, it is driven from the tube and receivers by a current of dry air or carbon dioxide; the apparatus is then disconnected. The boat containing the chlorides of copper, lead, and iron is allowed to slide into a dish or wide test tube, the combustion tube washed several times with hot water, and the chlorides dissolved in the washings from the tube by warming with addition of hydrochloric acid. The solution is evaporated with sulphuric acid, etc., and the lead estimated as sulphate; the copper is precipitated in the filtrate by sulphuretted hydrogen, and the iron in the filtrate from the copper sulphide by ammonia after oxidation with bromine water. The contents of the receiver are washed into a large beaker, and sulphuretted hydrogen passed into the warmed solution for a long time (the arsenic is only very slowly precipitated). The precipitate is filtered off and washed with dilute sulphuretted hydrogen water containing some ammonium acetate and acetic acid. Any bismuth and mercury present will be recognised by the dark colour of the precipitate. If present, the precipitate is washed off the filter paper, digested with ammonium sulphide, filtered through the same paper, washed with hot water containing ammonium sulphide, and the pure sulphides of tin, antimony, and arsenic (with sulphur) reprecipitated by acidifying with sulphuric acid and warming on a boiling water-bath. The separation of the tin, antimony, and arsenic is carried out as follows:—The sulphides are treated with fuming hydrochloric acid and a small quantity of potassium chlorate, gently warmed, so that the separated sulphur does not melt until it is quite white, the solution filtered through an asbestos filter, which is washed with strong hydrochloric acid, and in the cooled, strong hydrochloric acid solution the arsenic is precipitated as sulphide by passing sulphuretted hydrogen (for one hour). The precipitated sulphide is filtered off on to an asbestos filter, washed first with strong hydrochloric acid, then with boiled water,

dissolved in ammonia, the solution evaporated, the residue oxidised with nitric acid or chlorine water, evaporated, and the arsenic finally weighed as magnesium pyroarsenate,  $\text{Mg}_2\text{As}_2\text{O}_7$ , or as silver arsenate,  $\text{Ag}_3\text{AsO}_4$ . Generally, only very small quantities of arsenic are estimated as silver arsenate (*cf.* p. 273). The sulphuretted hydrogen in the strongly acid filtrate from the arsenic sulphide is decomposed by a few crystals of potassium chlorate, the solution brought into a porcelain dish, diluted with a little water, and the antimony precipitated by digesting on the water-bath with pure iron.

Absolutely pure iron for this purpose is prepared as follows:—A dilute solution of ferrous chloride is precipitated with oxalic acid, the yellow oxalate completely washed by decantation with water, dried, converted into ferric oxide by ignition in a muffle, and this reduced by igniting in a current of pure hydrogen in a porcelain tube. The spongy, grey iron so obtained is specially suited to the separation of antimony from tin by Tookey's method. In case perfectly pure iron is unobtainable, iron or steel turnings free from copper, or piano wire may be used.

At the end of half an hour the precipitation of the antimony, as a black powder, is complete; the solution is further warmed until only a little iron is left undissolved, the antimony filtered off on to a paper on which a few centigrams of iron are placed, and washed with boiled water strongly acidified with hydrochloric acid. The filtrate is nearly neutralised with ammonia, diluted, the tin precipitated by passing in sulphuretted hydrogen, as dark brown stannous sulphide, which is filtered off, washed with dilute sulphuretted hydrogen water in which a few grams of ammonium sulphate are dissolved, dried, and converted into stannic oxide by ignition in a porcelain crucible. After igniting for some time, a piece of ammonium carbonate about the size of a pea is added to the contents of the crucible, the lid replaced, and again strongly ignited so as to obtain the stannic oxide free from sulphuric acid.

The antimony is dissolved in hydrochloric acid and a little potassium chlorate, the solution, to which some tartaric acid is added, strongly diluted, sulphuretted hydrogen passed in, and the antimony sulphide obtained weighed as oxide,  $\text{Sb}_2\text{O}_4$ .

For the separation of the sulphides insoluble in ammonium sulphide (mercury and bismuth sulphides), hot, dilute nitric acid is poured over the filter paper, and the bismuth precipitated as carbonate by neutralising the solution with ammonia, adding ammonium carbonate, and warming. The carbonate is finally weighed as bismuth oxide (*cf.* Bismuth, p. 243). Any mercury sulphide remaining undissolved is dissolved in aqua regia, and precipitated as mercurous chloride by phosphorous acid ( $\text{PCl}_3$  and water). It is filtered off on to a weighed filter paper, dried, and weighed as mercurous chloride.  $\text{Hg}_2\text{Cl}_2 \times 0.8493 = \text{Hg}_2$ .

The mercury may be more accurately determined by heating 5 g. of the alloy in a porcelain boat placed in a porcelain tube in a current of hydrogen, and estimating the loss on ignition. Mercury, however, is but seldom found in white-metals, and is also a useless addition.

*Alloys containing much Lead*, recognisable by the colour of the fracture or of the turnings, and by the high specific gravity, are not suited to the treatment with chlorine, as they are very inclined to spit on warming in the current of chlorine. Such alloys are best analysed by the method described below under (b). A high content of lead in the alloy is recognised by the voluminous separation of lead chloride on dissolving a few decigrams in aqua regia, cooling, and adding absolute alcohol.

*Alloys containing Zinc*.—The method described under (e), p. 263, is to be recommended.

(b) *Metal for Bearings, Type-metal, Stereotype-metal, etc.*—One gram of the finely divided metal is dissolved, without heating, in 15 c.c. of fuming hydrochloric acid with the addition of strong nitric acid (sp. gr. 1.4), drop by drop. Alloys containing 80 per cent. and over of lead in the form of very fine turnings are treated with aqua regia (prepared from dilute acids, 30 c.c. for 1 g. of metal) and gently warmed for a long time on the water-bath. Nitric acid is then added until the solution becomes distinctly yellow, if copper is present until the colour is yellowish green; aqua regia, previously warmed until chlorine commences to be evolved, is also very suitable for the dissolving of the alloy. To the solution so obtained, ten times its volume of absolute alcohol is added in small quantities at a time, thereby precipitating lead chloride in large, easily filtered crystals; only about 1 mg. of lead remains in solution as chloride. The lead chloride is then washed carefully with alcohol, and as little as possible brought on to the filter paper. After drying, the lead chloride is shaken into a large weighed crucible, any adhering to the glass washed with hot water into the crucible, the filter paper washed with hot water, the combined solutions evaporated on the water-bath, the residue dried in the air-bath at  $150^{\circ}$  for three hours, and the lead chloride weighed.  $\text{PbCl}_2 \times 0.7449 = \text{Pb}$ .

The alcohol in the filtrate from the lead chloride is driven off by evaporation, 1 g. of tartaric acid as ammonium tartrate added, the solution made distinctly ammoniacal, sulphuretted hydrogen water added in small quantities until no further precipitate is formed, and warmed on the water-bath, which causes the precipitate (consisting of sulphides of copper, bismuth and mercury, and traces of sulphides of lead and iron) to coalesce. By this method (Finkener's) copper, bismuth, etc., are removed from the solution; their separation and estimation are carried out as described above under (a).

After acidifying the filtrate with hydrochloric acid, tin and antimony are precipitated as sulphides by sulphuretted hydrogen.



The mixture of tin and antimony sulphides is dissolved in hydrochloric acid and potassium chlorate, the separation carried out by means of iron (as given under (a)), the antimony containing iron dissolved, reprecipitated by sulphuretted hydrogen, the antimony sulphide, which always contains some chlorine, dissolved in ammonium sulphide, reprecipitated by warming with dilute sulphuric acid or acetic acid, washed off the filter paper into a dish, and evaporated to dryness on the water-bath. The antimony sulphide adhering to the filter paper is dissolved off in ammonium sulphide, the solution allowed to run into the dish, again evaporated, the dish removed from the water-bath, covered with a clock-glass, and fuming nitric acid run on to the residue from a pipette. The antimony sulphide is immediately oxidised without separation of sulphur, and after warming for a short time the contents of the dish are washed with a little water into a weighed porcelain crucible, evaporated, the sulphuric acid driven off on a sand-bath, the residue strongly ignited and weighed as oxide.  $\text{Sb}_2\text{O}_4 \times 0.7898 = \text{Sb}$ .

In the filtrate from the metallic antimony the tin is precipitated as described under (a), and finally weighed as stannic oxide.  $\text{SnO}_2 \times 0.7881 = \text{Sn}$ .

In these alloys, arsenic (from the commercial antimony) is generally only found in traces. If it is to be estimated, a separate weighing of several grams is dissolved in hydrochloric acid and potassium chlorate, any separated lead chloride filtered off, strong hydrochloric acid added, sulphuretted hydrogen passed in, and the copper sulphide, together with arsenic sulphide as impurity, filtered off through an asbestos filter. After washing with hot water, the small amount of arsenic sulphide is dissolved out with hot ammonia, the solution evaporated in a porcelain dish, oxidised with strong nitric acid, and the arsenic precipitated as ammonium magnesium arsenate. The trace of copper which is dissolved remains unprecipitated in the ammoniacal solution.

(c) *Alloys containing less than 15 per cent. of Lead and Copper.*—If it be desired to avoid the treatment with chlorine, 1 g. of the alloy rich in tin is dissolved in hydrochloric acid and potassium chlorate, 13 g. of tartaric acid as ammonium tartrate added, the diluted solution saturated with ammonia, and the copper and lead then precipitated by careful addition of sulphuretted hydrogen water; the further treatment of the precipitate is carried out as described under Tin (p. 258). In this case iron and also perhaps zinc are found in the precipitate. Tin and antimony are precipitated in the filtrate by acidifying with hydrochloric acid and passing sulphuretted hydrogen, and are separated by means of iron, etc., as given above.

(d) *Alloys free from Lead* (H. Nissenson and F. Crotochino<sup>1</sup>).—Half a gram of the alloy, as finely divided as possible, is placed in an

<sup>1</sup> *Chem. Zeit.*, 1902, **26**, 984; *J. Soc. Chem. Ind.*, 1902, **21**, 1350.

Erlenmeyer flask of 200 to 300 c.c. capacity, about 7 c.c. of concentrated sulphuric acid poured on and heated, till the evolution of gas ceases and the alloy is dissolved, which takes but a few minutes. The solution is cooled and carefully diluted with hot water, and the yellow precipitate, which forms immediately, allowed to settle whilst hot. This contains both tin and antimony, the latter as an antimonious salt. On oxidation, preferably by means of ammonium persulphate, the precipitate is rendered more easy of filtration, but even without this it is still easier to deal with than when oxidised by means of nitric acid. After washing, which may be neglected if other metals are not present, the paper and precipitate are ignited and the mixture of tin and antimony oxides weighed after strong ignition. The filtrate is tested for iron, cadmium, zinc, etc.

A second weighing of 0.5 g. is dissolved in sulphuric acid, cooled, a little hot water added, then 15 c.c. of dilute hydrochloric acid, and the antimony precipitated with iron wire; the precipitation is complete in a very short time. The separated antimony and copper is dissolved in hydrochloric acid and a few drops of nitric acid, precipitated with sulphuretted hydrogen, and the antimony sulphide dissolved in sodium sulphide and the solution electrolysed. The sulphides remaining undissolved may then be dissolved in nitric acid and tested for copper, bismuth, etc.

(e) *Alloys containing Lead* (H. Nissenson and F. Crotofino<sup>1</sup>).—If only tin and lead are to be determined, the alloy is treated with concentrated sulphuric acid by warming on the sand-bath or over a free flame, which acts the more easily the higher the content of tin and antimony and the smaller the amount of copper present, the contents of the flask cooled, treated with some hot water and a considerable quantity of ammonium oxalate, allowed to cool slowly, and the precipitate of lead sulphate filtered off. The tin is estimated in the filtrate by electrolysing the hot solution diluted to 180 c.c.

(f) *Determination of Lead*.—One gram of the fine turnings is gently warmed in a beaker with 15 c.c. of fuming hydrochloric acid, and a drop of strong nitric acid added from time to time. When the metal has dissolved, the solution is allowed to cool, the lead precipitated as chloride by adding three times the volume of absolute alcohol and stirring, filtered, after standing for twenty-four hours, and the lead chloride estimated as described on p. 244. In the filtrate from the lead chloride a small quantity of lead sulphate separates on the addition of sulphuric acid; this may be either neglected or estimated.

Ingots, as well as sheets of white-metal, are not homogeneous. In taking the sample (*cf.* p. 93), several ingots or sheets are drilled right through with a small drill, and the sample for analysis taken from the

<sup>1</sup> *Loc. cit.*

well-mixed drillings, or the block or ingot is sawn diagonally, the small pieces of metal mixed, and the sample taken as described on p. 93.

#### 4. Hard-Head.

This contains iron and arsenic, and may also contain antimony, tungsten, lead, aluminium, copper, sulphur, etc. In order to make an approximate determination of the tin, 1 g. of the very finely divided metal is dissolved in hydrochloric acid and potassium chlorate, the somewhat diluted solution saturated with ammonia, a large quantity of ammonium sulphide added, digested for a long time, filtered (tin, antimony, arsenic, together with molybdenum and tungsten), precipitated, separated as above, and the impure stannic oxide, containing some tungstic and molybdic acids finally weighed. R. Fresenius and E. Hintz<sup>1</sup> have described a more accurate method for the analysis of hard-head.

#### 5. Phosphor-Tin.

This comes into commerce in dark grey blocks which show a crystalline fracture, and contain up to 10 per cent. of phosphorus, usually 4 per cent.; it is used in the manufacture of phosphor-bronze.

For the analysis, 0.5 g. of fine borings are covered in a large beaker with 15 c.c. of fuming hydrochloric acid in which a large quantity of potassium chlorate has been dissolved by shaking in the cold. The contents of the beaker are swirled round, some more solid potassium chlorate added, gently warmed, diluted to 200 c.c., all the tin precipitated as sulphide by passing in sulphuretted hydrogen for a long time, the beaker placed on a boiling water-bath for half an hour, the tin sulphide filtered off and washed with very dilute sulphuretted hydrogen water, to which ammonium acetate and acetic acid are added. The dried sulphide is removed as completely as possible from the paper, the paper ignited in a weighed porcelain crucible, the sulphide added, heated with a small flame, then more strongly, and finally ignited, after the addition of a small piece of ammonium carbonate. The stannic oxide so obtained is weighed. The filtrate is evaporated down to about 30 c.c., and after the addition of magnesia mixture, saturated with ammonia. After six hours the ammonium magnesium phosphate is filtered off, washed with dilute ammonia (1:2), dried and removed from the filter paper; the portion that remains adhering to the paper is dissolved off in warm, dilute nitric acid, the solution evaporated in a weighed porcelain crucible, the dry ammonium magnesium phosphate added, very slowly heated over a Bunsen burner, and finally ignited over the blowpipe, the lid being placed on for the final strong ignition. The magnesium pyrophosphate so obtained is weighed.  $\text{Mg}_2\text{P}_2\text{O}_7 \times 0.2785 = \text{P}$ .

<sup>1</sup> *Z. anal. Chem.*, 1835, 24, 412; *J. Chem. Soc. Abstr.*, 1886, 50, 180.



For the determination of the phosphorus, Hempel<sup>1</sup> heats a few decigrams of the sample in a current of chlorine, absorbs the chlorides in a small receiver containing 10 c.c. of nitric acid (sp. gr. 1.4), washes the receiver out with a mixture of one volume of strong nitric acid and two volumes of water, and precipitates the phosphoric acid with ammonium nitromolybdate solution as described under phosphor-copper (p. 205).

### 6. Tin Waste and Ashes.

The ashes and waste produced by tinning iron (in the manufacture of tinplate), copper, brass, and bronze by dipping in the molten metal, which contain a quantity of tin (as stannous and stannic compounds and metal), as well as iron and copper oxides mixed with coke and sal-ammoniac, are included under this heading.

L. Rürup<sup>2</sup> recommends Kerl's method<sup>3</sup> for the analysis. An average sample of 500 g. weight is mixed intimately with 100 g. of tartaric acid, 400 g. of sodium carbonate, and 60 g. of chalk in a correspondingly large Hessian crucible, a covering of sodium carbonate and 100 g. of borax added, the crucible placed in a coke fire in a wind-furnace with a good draught, and the covering brought to a limpid fluid condition in half an hour or longer. The crucible is then removed from the fire, and cooled by means of an air blast from a water-pump for twenty minutes, or until it has sufficiently cooled down so that it can be completely cooled by placing in water. The crucible is then broken and the metallic button cleared from slag and weighed. The button is then drilled in several places, 1 g. of the drillings weighed off, decomposed with nitric acid (*cf.* Analysis of Bronze, p. 208), the stannic acid separated, the filtrate evaporated with sulphuric acid, and the copper separated electrolytically. The dried stannic acid is ignited and weighed. (In the description of the method as given by Rürup, the stannic acid contains a large quantity of iron, which is disregarded in the above case.)

W. Witter takes proportional quantities of the coarsely and finely ground sieved tin ashes and waste, weighs off an average sample of 25 g., mixes with 5 per cent. of powdered charcoal and potassium cyanide (from 50 to 100 g.), and fuses the mixture in a crucible in a wind-furnace. Drillings of the weighed button are taken and the content of tin determined either by gravimetric or volumetric methods.

### 7. Tin Dross.

This consists of very impure tin resulting from the prolonged use of tin for tinning copper, etc., by immersion in the molten metal, and

<sup>1</sup> *Ber.*, 1889, 22, 2478; *J. Chem. Soc. Abstr.*, 1890, 58, 83.

<sup>2</sup> *Chem. Zeit.*, 1896, 20, 406; *J. Chem. Soc. Abstr.*, 1897, 72, 234.

<sup>3</sup> *Metallurgische Probierkunst.*, 2nd ed., p. 482.

contains copper, zinc, iron, etc. On renewal of the bath this alloy is ladled off and run into ingots.

For the analysis, several ingots are drilled through, and 1 g. weighed off and analysed in the same way as bronze; a somewhat high content of iron oxide in the ignited stannic acid is recognised by a brown coloration.

### 8. Tin Slags.

W. Witter fuses 1 g. of the very finely ground slag with 5 g. of sodium hydroxide in a nickel crucible, dissolves the melt in water, acidifies the solution with hydrochloric acid, precipitates the tin by sulphuretted hydrogen, filters off the sulphide, washes it, dissolves it in ammonium sulphide, filters, etc., and finally weighs the stannic acid obtained. If the slag contains antimony, the separation from tin is carried out by means of iron according to Tookey-Clark's method (p. 260). After dissolving the melt in water and acidifying with hydrochloric acid, the solution may be reduced with iron or nickel, and titrated with iodine (*cf.* Pearce-Low and Darroch and Meiklejohn's methods, p. 257).

## VOLUMETRIC METHODS OF ESTIMATION<sup>1</sup>

Volumetric methods for the estimation of tin are coming largely into use, owing to the fact that they can be carried out much more rapidly than the gravimetric methods, and at the same time, with careful work, are capable of giving very good results. The following are the methods most often used:—

1. Titration of stannous chloride with ferric chloride solution.
2. Titration of stannous chloride with iodine in acid solution.
3. Titration of stannous chloride with iodine in alkaline solution.
4. Solution of metallic tin in ferric chloride and titration with potassium permanganate or potassium bichromate.

### 1. The Ferric Chloride Method.

This method is based on the fact that when ferric chloride is added to a concentrated, hot hydrochloric acid solution of stannous chloride, it is immediately reduced to ferrous chloride, stannic chloride being produced at the same time. One drop in excess of the ferric chloride serves to indicate the end-point by giving a decided yellow colour to the previously colourless solution, the colour being more marked the hotter and the more strongly acid the solution remains. The presence of chloride of lead, zinc, aluminium, ferrous iron, cobalt, nickel, antimony (antimonic), copper (cuprous), and cadmium, does not interfere with the process. Large quantities

<sup>1</sup> *Cf.* Parry, *Assay of Tin and Antimony*, p. 20.

of cobalt chloride and nickel chloride give highly coloured solutions which render the recognition of the end-point difficult, but this may be overcome to some extent by diluting the solution with hot water. Bismuth chloride and mercuric chloride are reduced to metal by stannous chloride, and must, therefore, be removed by separation with iron. Precipitated antimony, copper, arsenic, and the blue oxide of tungsten are attacked by the hot acid solution of ferric chloride, and must not be present; titanium must also be absent.

The standard solution, which must be free from nitric acid and arsenic, is made up either from pure iron or by dissolving 150 g. of ferric chloride in water, adding 300 to 500 c.c. of hydrochloric acid, and diluting to 2 litres. It is standardised by dissolving 1 g. of pure tin in 200 c.c. of concentrated hydrochloric acid in a 250 c.c. flask fitted with a rubber cork and bent glass tube leading into water, to prevent oxidation. This is boiled until solution is complete and the solution titrated at once.

In the case of alloys containing tin, lead, zinc, aluminium, iron, cobalt, and nickel, which are soluble in hydrochloric acid, but not containing antimony, arsenic, and copper, the determination is carried out as follows:—One gram of the finely divided alloy is weighed into a 250 c.c. flask fitted with a rubber cork and leading tube, 180 c.c. of pure hydrochloric acid added, and the flask heated on a sand-bath, but not boiled too rapidly, or the acid becomes too dilute before it has had time to thoroughly attack the metal; nor should it come to the boil too slowly, as in this case the metal may be completely attacked whilst there is still air in the flask, with the formation of stannic chloride. When solution is complete, the resulting liquid is titrated directly with the ferric chloride solution.

With alloys containing tin, lead, antimony, and but little copper and arsenic, 1 g. of the finely divided alloy is boiled with 50 to 75 c.c. of hydrochloric acid until action ceases; solution is completed by the cautious addition of a saturated solution of potassium chlorate. The excess of chlorine is boiled off and the solution reduced by the addition of piano wire. The action in the hot solution is rapid—arsenic, antimony, and copper being precipitated; one minute after the solution turns colourless, a thin strip of copper foil is added. When a freshly added strip of copper remains bright for one or two minutes, the solution is diluted with 50 to 60 c.c. of hot, boiled water and filtered rapidly into another flask, the precipitate being kept as far as possible out of contact with the air. The flask and paper are washed once with hot dilute hydrochloric acid. Excess of strip zinc is added to the solution to precipitate the tin, and when all action has ceased, a little of the liquid is poured into a beaker containing sulphuretted hydrogen water; a white precipitate indicates that all the tin is precipitated



The solution is poured off from the precipitated tin as completely as possible after any floating particles have been allowed to settle, and the remaining metal is dissolved in 180 c.c. of hydrochloric acid in a flask as before; the resulting solution is then titrated.

This method may be used for the estimation of tin in solutions obtained from any material, by first separating the metals precipitated by sulphuretted hydrogen in a hydrochloric acid solution, dissolving the precipitate in hydrochloric acid with the addition of potassium chlorate, and treating the solution as above with iron wire and metallic zinc.

## 2. The Iodine Method in Acid Solution.<sup>1</sup>

This method is very suitable for the analysis of white-metal alloys, the tin being readily estimated by reducing the hot solution of the chloride, cooling in an atmosphere of carbon dioxide, and titrating with iodine in the presence of starch. The reduction may be conveniently effected by means of iron<sup>2</sup> or nickel.<sup>3</sup> If antimony, arsenic, or copper be present, they will be precipitated, and will not interfere under the conditions of the assay. A modification of the method consists in reducing the stannic chloride with finely divided metallic antimony.<sup>4</sup> The reduction of 0.15 g. of tin is complete after one minute's boiling, and the excess of antimony which remains undissolved acts as a safeguard during the cooling, since it reduces any tin which may have become oxidised whilst the solution is still hot. Cold solutions of stannous chloride oxidise less readily. The presence of iron, chromium, nickel, cobalt, zinc, manganese, aluminium, bismuth, phosphorus, and sulphur is without effect on the results. Copper is reduced to cuprous chloride, and if the iodine be added in drops to the vigorously agitated solution, so as to prevent the formation of a local excess of iodine, accurate results may be obtained. Lead is without effect if sufficient hydrochloric be present to prevent the formation of lead iodide. Mercury is reduced to the metallic state, but is not oxidised in cold solutions. If molybdenum or tungsten be present, a coloured lower oxide is formed, which interferes with the end reaction; these metals should, therefore, be separated. Arsenic interferes seriously if more than one part in two hundred parts of tin be present.

The reduction by means of iron (Parry) is carried out as follows:—Half to one gram of the finely divided alloy is dissolved in hydrochloric acid with the addition of potassium chlorate to aid the solution; after dilution, the chlorine is boiled off and a clean piece of iron rod is

<sup>1</sup> S. W. Young, *J. Amer. Chem. Soc.*, 1897, **19**, 809; *J. Chem. Soc. Abstr.*, 1898, **74**, 192.

<sup>2</sup> Parry, *Assay of Tin and Antimony*, 1904, p. 23.

<sup>3</sup> Beringer, *Text Book of Assaying*, 1910, p. 288.

<sup>4</sup> Ibbotson and Brearly, *Chem. News*, 1901, **84**, 167.

placed in the solution, resting against the side of the beaker, which is covered with a watch-glass. The whole is heated to  $80^{\circ}$  to  $90^{\circ}$  for twenty to thirty minutes after the solution has become colourless. The solution is cooled, and when cold the watch-glass and iron rod are washed rapidly with a little cold, boiled water, starch added, and the solution titrated rapidly with iodine. It is not necessary to remove the precipitate of antimony, arsenic, and copper. The volume of the solution should not exceed 50 c.c., the quantity of hydrochloric acid being about one-fifth of the total volume, and the amount of tin present not more than 0.5 g.

The iodine solution recommended is made up by dissolving 21.32 g. of iodine and 45 g. of pure potassium iodide in a little water, and diluting to 1 litre.

The following method is adopted when the reduction is effected with antimony.<sup>1</sup> One gram of the alloy is dissolved in hydrochloric acid with addition of potassium chlorate, the chlorine boiled off, and the solution diluted to 100 c.c. An aliquot portion of the solution, which contains about 0.15 g. tin, is measured out and run into a flask; this is diluted to about 150 c.c. with water containing one-fifth of its volume of hydrochloric acid, heated, a little antimony added, and the whole boiled. The flask may be fitted with a rubber cork and leading tube. After boiling for a minute or two, the solution is cooled, starch added, and titrated with decinormal iodine. One c.c.  $N/10$  iodine solution = 0.00595 g. Sn.

### 3. The Iodine Method in Alkaline Solution.

According to Lenssen,<sup>2</sup> Rochelle salt and a solution of sodium bicarbonate are added to the solution of stannous chloride, which is then titrated with iodine in presence of starch paste, until the production of the blue colour. 253.84 g. I = 119 g. Sn.

### 4. The Indirect Ferric Chloride Method.

In this method either a solution of stannous chloride or of metallic tin is added to a hot hydrochloric acid solution of ferric chloride, and the ferrous chloride formed is estimated by titration.

## ELECTROLYTIC DETERMINATION OF TIN<sup>3</sup>

M. Heidenreich deposits the tin from a hot oxalate solution, acidified with oxalic acid, in a coppered Classen dish, and obtains in four to

<sup>1</sup> Ibbotson and Brearly, *Chem. News*, 1901, 84, 167.

<sup>2</sup> *J. prakt. Chem.*, 1908, 78, 200.

<sup>3</sup> Cf. *Quantitative Analysis by Electrolysis*, A. Classen, translated by B. Boltwood, p. 212; *Electro-Analysis*, E. F. Smith, p. 95; Heidenreich, *Ber.*, 1895, 28, 1586; *J. Soc. Chem. Ind.*, 1896, 15, 744; C. Engels, *Ber.*, 1895, 28, 3187; *J. Soc. Chem. Ind.*, 1896, 15, 219.

four and a half hours an adhesive deposit of silvery looking metal. To the solution (about 150 c.c.), containing about 0.3 g. of tin, 4 g. of ammonium oxalate are added, the solution acidified with 9 to 10 g. of oxalic acid, warmed to 60° to 65°, and electrolysed with a current of 1 to 1.5 ampère per 100 sq. cm. of cathode surface. The washing must be done without breaking the circuit. The dish is rinsed with water and alcohol, and dried at 80° to 90°.

## ARSENIC

Only a very small proportion of the compounds of arsenic which find their way into commerce are obtained directly from ores of arsenic; by far the greater quantity are obtained as by-products from the crude arsenious acid (white arsenic) recovered from the settling flues in the roasting of ores containing arsenic.

**Arsenic Ores** proper include:—

*Native Arsenic (Flaky Arsenic)*, often containing antimony and silver, as well as a little iron, less frequently nickel and cobalt.

*Arsenical Pyrites (Mispickel)*,  $\text{FeS}_2 + \text{FeAs}_2$ , with 46 per cent. of arsenic, 34.4 per cent. of iron, and 19.6 per cent. of sulphur. Frequently found together with tin-stone, iron pyrites, copper pyrites, galena, zinc blende, fahl ore, etc.

*Arsenical Iron (Leucopyrite)*,  $\text{FeAs}_2$ , with 72.8 per cent. of arsenic, and *Löllingite*,  $\text{Fe}_2\text{As}_3$ , with 66.8 per cent. of arsenic; not unfrequently containing some gold. The ore from Reichenstein contains 0.0022 to 0.0024 per cent. of gold.

The natural sulphides of arsenic—*Realgar*,  $\text{AsS}$ , and *Orpiment*,  $\text{As}_2\text{S}_3$ , are used as found.

Arsenic is also found in many other ores, such as Speiss cobalt, Kupfer nickel, etc., from which it is partially recovered by metallurgical treatment.

The products most frequently met with in analysis are:—Ores of arsenic, metallic arsenic, white arsenic, and red and yellow arsenic sulphides. The detection of arsenic in colours, etc., and in commercial crude acids (sulphuric and hydrochloric acids), is of special importance.

*Dry Assay of Arsenic*.<sup>1</sup>—This is employed for estimating the available quantity of arsenic, arsenious acid, or sulphur compounds of arsenic in ores.

### I.—GRAVIMETRIC METHODS OF ANALYSIS

Arsenic is determined either as trisulphide ( $\text{As}_2\text{S}_3$ ), pentasulphide ( $\text{As}_2\text{S}_5$ ), magnesium pyroarsenate ( $\text{Mg}_2\text{As}_2\text{O}_7$ ), or as silver arsenate

<sup>1</sup> Cf. C. and J. J. Beringer, *Text Book of Assaying*, 12th ed., 1910, p. 382; Rhead and Sexton, *Assaying and Metallurgical Analysis*, 1902; Kerl, *Probierebuch*, 3rd ed., p. 170.



( $\text{Ag}_3\text{AsO}_4$ ). The determination as hydrated ammonium magnesium arsenate cannot be recommended.

### 1. Estimation as Trisulphide, $\text{As}_2\text{S}_3$ .

The arsenic may be separated from solutions of arsenious acid (*e.g.*, in hydrochloric acid) as trisulphide, provided no substances are present which exert an oxidising action on the sulphuretted hydrogen. Such a solution is obtained, for instance, by distilling the arsenic as arsenious chloride (*cf.* Vol. I., p. 284, and Vol. II., p. 21), and condensing the distillate (arsenious chloride and hydrochloric acid) in water free from air. By carefully passing in sulphuretted hydrogen all the arsenic is precipitated as trisulphide; any traces of admixed sulphur may be extracted by means of hot alcohol, after collecting the precipitate on a filter paper dried at  $100^\circ$ , and washing with water. The precipitate and paper are dried at  $100^\circ$  to  $110^\circ$  till constant, and weighed.  $\text{As}_2\text{S}_3 \times 0.6093 = \text{Arsenic}$ .

Small quantities of arsenic trisulphide are dissolved in ammonia, the solution evaporated, the residue oxidised with fuming nitric acid, and the arsenic pentoxide produced estimated as magnesium pyroarsenate or as silver arsenate.

### 2. Estimation as Pentasulphide, $\text{As}_2\text{S}_5$ .

Arsenic is estimated as pentasulphide when to the solution of the mixed sulphides (*cf.* Separation from Tin and Antimony, p. 284) in hydrochloric acid and potassium chlorate, a large quantity of strong hydrochloric acid is added, and sulphuretted hydrogen passed in for a long time in the cold. It is collected on a dried asbestos filter (Gooch crucible, *cf.* Vol. I., p. 25), washed first with strong hydrochloric acid containing sulphuretted hydrogen, then with boiling water, and finally with hot absolute alcohol, and weighed, after drying at  $100^\circ$  to  $110^\circ$ , till constant.  $\text{As}_2\text{S}_5 \times 0.4832 = \text{Arsenic}$ .

F. Neher<sup>1</sup> recommends the use of a solution containing one volume of water and two volumes of fuming hydrochloric acid of sp. gr. 1.2, in the separation of arsenic from antimony, bismuth, lead, etc.; more hydrochloric acid retards the precipitation, which is usually completed by a rapid current of sulphuretted hydrogen in one hour. Warming must be avoided; in fact, after the addition of the strong hydrochloric acid, it is well to cool. If the solution, after standing corked in a flask for two hours, still smells strongly of sulphuretted hydrogen, one may be certain that the precipitation is complete.

In presence of stannic chloride, a compound containing tin, which is quite insoluble in hydrochloric acid, separates with the arsenic pentasulphide.

<sup>1</sup> *Z. anal. Chem.*, 1893, **32**, 45; *J. Chem. Soc. Abstr.*, 1893, **64**, 186.

This method of estimation was first published by Le Roy W. M'Cay.<sup>1</sup>

Both the trisulphide and the pentasulphide of arsenic may be dissolved off the filter paper by pouring on a warmed mixture of ammonia and hydrogen peroxide; in the cooled solution the arsenic acid is precipitated as usual with magnesia mixture, ammonia, and alcohol. Perfectly pure hydrogen peroxide is now easily obtainable.

### 3. Estimation as Magnesium Pyroarsenate, $\text{Mg}_2\text{As}_2\text{O}_7$ .

Arsenic is frequently precipitated and (in presence of tartaric acid) also separated from antimony and tin as this compound. The sulphides of arsenic, antimony, and tin are dissolved by gently warming with hydrochloric acid and potassium chlorate (the sulphides of arsenic are treated with fuming nitric acid), and the temperature raised, but not sufficiently to melt the nearly white undissolved sulphur. If antimony and tin are present, some tartaric acid is added to the solution, which is then somewhat diluted, filtered through a small paper into a beaker, and the paper washed with a little water.

Sufficient magnesia mixture (prepared by dissolving 110 parts of crystallised magnesium chloride and 140 parts of ammonium chloride in 1300 parts of water and 700 parts of strong ammonia) is then added, the solution saturated with ammonia, one-quarter of the volume of absolute alcohol added, swirled round and allowed to stand covered, under a bell jar, for forty-eight hours. At the expense of accuracy, but without introducing any appreciable error, the precipitate may be filtered off after six to twelve hours and washed with a mixture of two volumes of strong ammonia with two volumes of water and one volume of alcohol. The precipitate and paper are dried in an air-bath, the precipitate removed as completely as possible on to glazed paper, the paper replaced, in the funnel, hot, dilute nitric acid poured over it, the solution evaporated in a weighed porcelain crucible, the precipitate then introduced into the crucible, the lid placed on, the contents gently heated to drive off the ammonia and water, and the temperature gradually increased up to a dull red heat; the lid is then removed, and the crucible and its contents strongly ignited by means of a blowpipe or large Bunsen burner. If the crucible be ignited with the lid on, a considerable amount of arsenic may be volatilised owing to reduction by means of the burner gases. The crucible, whilst still hot, above  $100^\circ$ , is placed in a desiccator containing sulphuric acid and weighed with the lid after half an hour.  $\text{Mg}_2\text{As}_2\text{O}_7 \times 0.4829 = \text{As}$ .

### 4. Estimation as Silver Arsenate, $\text{Ag}_3\text{AsO}_4$ .

If a solution of arsenic acid, free from chlorides, is nearly neutralised with ammonia, silver nitrate solution added, and then just neutralised

<sup>1</sup> *Chem. News*, 1886, 54, 287.

with ammonia, a chocolate-brown precipitate of silver arsenate is produced, which settles well on warming. The precipitate is washed by decantation, collected on a weighed filter paper, dried at  $100^{\circ}$  till constant, and weighed.  $\text{Ag}_3\text{AsO}_4 \times 0.1621 = \text{As}$ .

The weight of the arsenate may also be arrived at by bringing the precipitate into a weighed crucible, evaporating off the water, and drying the residue in an air-bath; it is still quicker to dissolve the washed arsenate in dilute nitric acid, add some ferric sulphate to the diluted solution, and estimate the silver by titration with ammonium thiocyanate standardised against silver (Volhard's method, p. 116).  $\text{Ag} \times 0.2317 = \text{As}$ .  $\text{Ag} \times 0.3059 = \text{As}_2\text{O}_3$ .

A good excess of silver nitrate is used, and the filtrate from the silver arsenate tested by adding a few drops of dilute ammonia, which should give no further brown coloration of silver arsenate. No silver oxide is precipitated in the slightly over-neutralised solution, since, according to Le R. W. M'Cay, it is soluble in small quantities in the solution containing ammonium nitrate.

On account of the high molecular weight and small percentage of arsenic in silver arsenate, Finkener dissolves small quantities of ammonium magnesium arsenate, after drying, in dilute nitric acid, evaporates the solution in a weighed porcelain crucible, adds excess of silver nitrate, and evaporates several times with 10 to 20 c.c. of water until a fresh addition of water produces no further formation of arsenate (or darkening of the silver arsenate); the arsenate is then washed by decantation, dried, and weighed. A small amount of silver chloride as impurity in the arsenate is recognised on dissolving the weighed silver arsenate in dilute nitric acid; the silver chloride may either be collected on a small filter paper, weighed as silver and deducted from the weight of the impure arsenate, or, the nitric acid solution of the arsenate may be titrated as stated above.

Any chlorides in the solution may be separated before neutralising with ammonia by the addition of silver nitrate and filtering off any silver chloride precipitated. Solutions containing sulphuric acid must be diluted on account of the slight solubility of silver sulphate.

##### 5. Estimation as Arsenic Pentoxide, $\text{As}_2\text{O}_5$ (Bäckström<sup>1</sup>).

On warming with fuming nitric acid, arsenic sulphide is converted into arsenic pentoxide and sulphuric acid. The solution is evaporated in a weighed porcelain crucible, the sulphuric acid driven off by carefully heating (*e.g.*, over a sand-bath) and the residual arsenic pentoxide heated to a dull red heat, insufficient to convert it into arsenious oxide. The hot crucible is placed in a desiccator containing phosphorous pentoxide, and is subsequently quickly weighed with the cover. After

<sup>1</sup> *Z. anal. Chem.*, 1892, **31**, 663.



weighing, the arsenic pentoxide is dissolved in hydrochloric acid and water and tested by means of barium chloride for any retained sulphuric acid.

The difficulty of this method lies in getting the right temperature, so that whilst all the sulphuric acid is driven off, no reduction of arsenic pentoxide to arsenious oxide takes place; otherwise the method would be extremely useful for technical determinations, such as the estimation of the arsenic in yellow and red arsenic (mixtures of sulphide of arsenic with arsenious acid).

## II.—VOLUMETRIC METHODS

### 1. Estimation of Arsenious Acid.

The best method is that of F. Mohr, which depends on the oxidation of the solution, rendered alkaline by sodium bicarbonate, by means of iodine, in presence of starch as indicator, in accordance with the equation:—



Stannous salts and antimonious acid should not be present; solutions of these, to which Rochelle salt is added and then made alkaline with sodium bicarbonate, may likewise be titrated with iodine solution (*cf.* p. 79).

For the preparation and standardisation of the iodine solution, *cf.* Vol. I., p. 113.

The solution to be titrated (*e.g.*, of white arsenic or flue dust, etc.) may conveniently contain 0.1 g. of arsenious oxide; it is neutralised with sodium carbonate, then 20 c.c. of a cold, saturated solution of sodium bicarbonate (prepared from the commercial salt, washed free from any adhering sodium carbonate by means of water) added, and titrated after the addition of starch solution. Alkaline solutions are first just acidified with hydrochloric acid, then sodium bicarbonate solution added, etc.

Solutions of arsenic acid are evaporated with sulphuric acid in order to drive off any nitric acid, the residue taken up with a large excess of a saturated aqueous solution of sulphur dioxide, gently warmed, the sulphur dioxide completely expelled by boiling, the solution cooled and neutralised, etc., as above.

H. Nissenson and A. Mittasch<sup>1</sup> titrate the arsenic and antimony together in the sulphuric acid solution of the sulphides by means of *N*/10 potassium bromate solution<sup>2</sup> (*cf.* Analysis of Hard Lead, p. 235), using a few drops of indigo solution as indicator. For the determination of the antimony a second weighing of 1 g. is treated with brom-hydro-

<sup>1</sup> *Chem. Zeit.*, 1904, **28**, 184; *J. Soc. Chem. Ind.*, 1904, **23**, 338.

<sup>2</sup> Györy, *Z. anal. Chem.*, 1893, **32**, 415; *J. Chem. Soc. Abstr.*, 1893, **64**, 554.

chloric acid and heated for a considerable time in the fume cupboard in order to drive off the arsenic; after diluting with water the antimony is precipitated by sulphuretted hydrogen. The sulphide is then dissolved in 50 c.c. of a cold, saturated solution of sodium sulphide, the solution heated to boiling, filtered into a platinum dish, boiling water added, and electrolysed for forty minutes with a current density of about 1.6 ampères per square decimetre. The results so obtained are thoroughly satisfactory.

## 2. Estimation of Arsenic Acid.

The method most to be recommended (that of Baedeker and Brügelmann) depends on the precipitation of the arsenic acid by a solution of uranyl acetate or uranyl nitrate ( $\text{UO}_2(\text{NO}_3)_2 + 6\text{H}_2\text{O}$ ), the end-point being recognised by means of spot tests with potassium ferrocyanide solution.

The uranium solution should contain about 20 g. of uranium oxide to the litre. For its standardisation a weighed quantity (about 0.2 g.) of arsenious oxide is dissolved in a flask by boiling with strong nitric acid, the solution evaporated, the residue dissolved in water, neutralised with sodium hydroxide or ammonia, strongly acidified with acetic acid, uranium solution run into the cold solution until the greater part of the arsenic pentoxide is precipitated, the solution heated to boiling for a few minutes, and then titrated further with the uranium solution until a red coloration is given with a drop of potassium ferrocyanide solution on a porcelain tile.

Since preliminary titrations are necessary for the standardisation, it is well to prepare a larger quantity of arsenic pentoxide or sodium arsenate solution; in the preliminary titration, the uranium solution is always added in portions of 2 to 5 c.c. at a time, and the solution then tested with the potassium ferrocyanide.

## III.—SPECIAL METHODS

### 1. For Ores, Speisses, and Waste, etc. (*cf.* also Vol. I., pp. 281 *et seq.*).

(a) One gram of the very finely ground substance is dissolved in aqua regia or in nitric and tartaric acids, the solution diluted, sulphuretted hydrogen passed in, the precipitate extracted with hot potassium sulphide solution, and the sulphides of arsenic, antimony, and tin reprecipitated by acidifying the cooled solution with dilute sulphuric acid. The mixed sulphides are dissolved in hydrochloric acid and potassium chlorate, the solution diluted, some tartaric acid added and the arsenic precipitated by addition of magnesia mixture (see I. 3), ammonia, and alcohol, and finally weighed as magnesium pyroarsenate.

The antimony and tin in the filtrate may be determined as given under the analysis of White-metals (p. 258).

(b) *F. Reich's and T. Richter's Method* (as employed at the Freiberg metallurgical works for raw and roasted ores).—Nitric acid (sp. gr. 1.2) is poured over 0.5 to 1 g. of the substance in a large porcelain crucible, which is covered with a watch-glass and heated on a sand-bath. After the decomposition, the watch-glass is removed and the contents of the crucible evaporated on the sand-bath. Three times the weight of pure anhydrous sodium carbonate (free from chloride) and an equal quantity of nitre are then added, and the crucible heated over a burner or in a muffle till tranquil fusion of the melt ensues. The cooled melt is extracted with hot water, the solution neutralised with nitric acid, the carbon dioxide driven off by warming, silver nitrate added, and then ammonia in very slight excess, which precipitates the arsenic acid as silver arsenate (according to Method I. 4, p. 272). The dried precipitate is removed from the paper, the paper ignited on a scorifying dish, the precipitate together with 10 to 20 g. of assay lead added, again scorified, and the lead button obtained cupelled on a cupel (*cf.* Silver Assay by Scorification, p. 98). From the weight of the silver bead obtained the amount of arsenic contained in the original substance may be calculated. One hundred grams of silver correspond to 23.17 g. of arsenic, or 30.59 g.  $\text{As}_2\text{O}_3$ .

Pearce boils the aqueous solution of the melt, acidified with nitric acid, neutralises after cooling with ammonia, filters off any precipitated aluminium compounds, precipitates the arsenic according to the method given under I. 4, p. 272, dissolves the silver arsenate in dilute nitric acid, and titrates the silver by Volhard's method.

Raw ores may also be mixed with ten times their weight of a mixture of equal parts of sodium carbonate and nitre, covered with a deep layer of the same mixture, and then fused.

(c) Fusion of the ground ore with six times its weight of a mixture of equal parts of sodium carbonate and sulphur, and lixiviation of the melt with hot water, etc. This method is less frequently used, generally only if lead, copper or antimony, and tin are to be determined in the sample as well as arsenic.

(d) *Wastes* are analysed by one of the foregoing methods, or more conveniently, after evaporation of their solution in aqua regia, and addition of ferrous chloride and fuming hydrochloric acid, the arsenic is volatilised by distillation as arsenious chloride (p. 196), and the arsenic in the distillate either determined as arsenic trisulphide (Method I. 1, p. 271), or titrated by Mohr's method (Volumetric Method II. 1, p. 274).

(e) *F. W. Boam's*<sup>1</sup> *Method for the Volumetric Determination of Arsenic in Ores, etc.*—One to one and a half gram of the finely ground

<sup>1</sup> *Chem. News*, 1890, 61, 219.



substance is heated with 20 to 25 c.c. of strong nitric acid, and the solution evaporated to dryness. After cooling, 30 c.c. of concentrated sodium hydroxide solution (30 per cent.) is poured on to the residue, boiled for a few minutes, some water added, filtered, and the filtrate diluted to 250 c.c. Twenty-five c.c. of this solution are acidified with 50 per cent. acetic acid in which 10 per cent. of sodium acetate is dissolved, heated to boiling, and titrated with uranium acetate solution (Volumetric Method, II. 2, p. 275). Boam uses a uranium solution of which 1 c.c. corresponds to 0.00125 g. of arsenic, prepared by dissolving 17.1 g. of pure uranyl acetate in 15 c.c. of strong acetic acid and water, and then making up the solution to 2 litres.

The method is applicable to all ores decomposed by nitric acid. Any ferric arsenate formed is completely decomposed by boiling with a large excess of sodium hydroxide.

(f) *Arsenic Ores* (native arsenic, arsenical pyrites, arsenical iron) and speisses are treated according to H. Nissenson and F. Crotogino<sup>1</sup> by heating with concentrated sulphuric acid as follows:—Five grams of the finest possibly ground speiss, dried at 100°, are placed in a round-bottomed or small Erlenmeyer flask, a small funnel placed in the mouth of the flask, 15 c.c. of strong sulphuric acid poured on, and the contents heated until the metallic appearance of the speiss has disappeared; the decomposition is ended, according to the temperature, nature, and fineness of the substance, in from half to three hours at the most. After cooling, hot water is added (by addition of cold water arsenious acid readily separates), and, after settling, the solution is filtered. The filtrate is heated to boiling, a rapid current of sulphuretted hydrogen passed in till the precipitate balls together, which generally takes place in about ten minutes, the solution filtered off into a 500 c.c. flask, and the precipitate washed well with hot water. The filtrate is boiled to expel sulphuretted hydrogen, the iron oxidised with a sufficient quantity of ammonium persulphate or hydrogen peroxide, 200 c.c. of ammonia added, and after again boiling and cooling, diluted to 500 c.c. One hundred c.c. of the solution are then filtered through a dry paper, and nickel and cobalt separated electrolytically in the usual way by diluting to about 180 c.c., and electrolysing the hot solution in a Classen dish with a current of 1 ampère per 100 sq. cm. for one to two hours, according to the amount of nickel and cobalt present. The sulphide precipitate is dissolved in hydrochloric acid and potassium chlorate, the chlorine driven off, the solution diluted to 500 c.c., 100 c.c. filtered off, neutralised with ammonia after addition of tartaric acid, and the arsenic precipitated as ammonium magnesium arsenate by means of magnesia mixture. The copper in the filtrate, if only present in very small quantity, is estimated colorimetrically; if present in larger

<sup>1</sup> *Chem. Zeit.*, 1902, 26, 847; *J. Chem. Soc. Abstr.*, 1902, 82, 695.

quantity, the filtrate is acidified with dilute sulphuric acid, the copper precipitated by boiling with sodium thiosulphate, the precipitate washed with boiling water, dried, ignited, and weighed as cupric oxide. If antimony is present, the sulphide precipitate is washed free from sulphuretted hydrogen, digested with ammonium carbonate solution to separate the arsenic, the residue extracted with 20 c.c. of concentrated sodium sulphide solution, and the antimony separated from the solution thus obtained electrolytically (*cf.* p. 282). For the determination of the copper, or bismuth and cadmium, the sulphides remaining on the filter paper are dissolved in nitric acid, etc. The treatment with concentrated sulphuric acid is especially suited for pyrites, copper pyrites, mixed zinc-lead ores, etc.

Silver in naturally occurring native arsenic is determined by scorification and cupellation (*cf.* pp. 98 and 105).

**2. For Sublimed Arsenic.**—This metallurgical product may contain as impurity particles of arsenical pyrites introduced during sublimation. Traces of sulphur are recognised by dissolving in aqua regia, evaporating, again evaporating with hydrochloric acid, and precipitating the hot dilute hydrochloric acid solution with barium chloride solution. Iron is determined as sulphide, FeS, by mixing a few grams of the sample with an equal weight of sulphur in a Rose's crucible, and heating gradually up to strong ignition in a current of hydrogen and then allowing the crucible to cool in the current of hydrogen.

**3. For Crude Arsenious Acid (White Arsenic) and Flue Dust.**—About 0.5 g. of the substance is dissolved in a flask by prolonged boiling with excess of potassium hydroxide. The solution, which is generally muddy owing to the presence of soot, sand, ferric oxide, etc., is cooled, diluted to nearly 100 c.c., and made just acid by adding hydrochloric acid, drop by drop. Fifty c.c. of a cold saturated solution of sodium bicarbonate is then added, the solution diluted to 500 c.c., in 25 c.c. of which the arsenious acid is titrated by F. Mohr's method (Volumetric Method II. 1, p. 274).

Commercial white arsenic is practically pure arsenious oxide, only being contaminated by extremely small quantities of flue dust (from the fuel of the roasting furnace) and traces of arsenic sulphide. Both are recognised by dissolving in hot hydrochloric acid, when the sulphide separates in a flocculent form. White arsenic, containing sulphur, if carefully sublimed in a porcelain dish, gives at the commencement a reddish deposit on another dish placed over it as a cover.

White arsenic glass is nearly chemically pure arsenious oxide.

**4. For Artificially prepared Realgar (Red Arsenic Glass) and Orpiment (Yellow Arsenic Glass).**—The composition of these products only approximates to that of the naturally occurring sulphides, arsenic

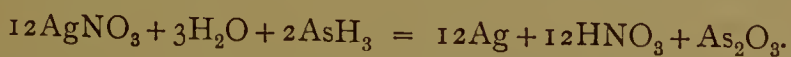
disulphide ( $\text{AsS}$ ) and arsenic trisulphide ( $\text{As}_2\text{S}_3$ ); for instance, yellow arsenic glass contains a considerable quantity of arsenious acid. Impurities (particles of ore, etc.) remain behind undissolved on boiling the finely ground substance with potassium hydroxide and sulphur. For the estimation of the sulphur, 0.1 g. to 0.2 g. of the substance is dissolved in aqua regia and the solution further treated as described on p. 278. For the determination of the arsenic, a small portion of the sample is boiled with concentrated nitric acid, the residue dissolved in water, and the arsenic pentoxide either precipitated with magnesia mixture (Method I. 3, p. 272) or titrated with uranium solution (Method II. 2, p. 275). Earthy impurities remain behind on volatilising a few grams in a crucible.

**5. In Rosaniline, Rosaniline residues, and Colouring Matters suspected of containing Arsenic.**—The arsenic is distilled as chloride, by mixing the substance with ferrous sulphate and a large quantity of common salt in a large flask, pouring on pure (arsenic free) sulphuric acid, warming the flask on a sand-bath, and condensing the vapours through a well-cooled, spiral condenser. In the case of rosaniline residues rich in arsenic, a small weight of the sample suffices. The arsenic in the distillate is either determined as trisulphide (Gravimetric Method I. 1, p. 271), or titrated by Mohr's method (Volumetric Method II. 1, p. 274).

**6. In Crude Commercial Hydrochloric and Sulphuric Acids.**—Acids containing arsenic evolve, when used for pickling iron, for preparing hydrogen, in the manufacture of zinc chloride from zinc ashes, etc., corresponding quantities of the highly poisonous arseniuretted hydrogen.

For the estimation of the content of arsenic, Prauss generates hydrogen from pure zinc, free from arsenic, and the diluted acid under examination. The gas is passed through a series of wash-bottles, containing a measured quantity of standard neutral silver nitrate solution, and after the experiment, the silver in the filtrate from the separated metallic silver is titrated with ammonium thiocyanate.

The decomposition of arseniuretted hydrogen takes place in accordance with the equation:—



Prauss found that the results obtained by this method are sufficiently accurate for technical purposes, *e.g.*, 0.10 per cent. instead of 0.12 per cent., as given by a gravimetric determination.

The arsenic may also be accurately determined by passing pure sulphuretted hydrogen (prepared from calcium sulphide or sodium sulphide and pure hydrochloric or sulphuric acid) for a long time into the diluted and gently warmed acid after reducing with sulphurous acid



and driving off the excess; the arsenic is thus precipitated as sulphide (*cf.* also Vol. I., pp. 383 and 414).

7. **Shot** (Arsenical Lead), *cf.* Lead, p. 239.

#### DETECTION OF ARSENIC

In many ores and metallurgical products, arsenic is contained in considerable quantities and is easily recognisable by blowpipe tests. When heated on charcoal in the blowpipe flame, a garlic-like odour is evolved, and when fused with sodium carbonate and potassium cyanide in a small glass tube sealed at one end, a dark brown metallic-looking mirror of arsenic is formed. The wet tests, such as the well-known Marsh-Berzelius test, are much more delicate; in carrying them out, only absolutely pure, specially tested reagents may be employed. These tests are fully described in Vol. I., pp. 362 *et seq.*

The substance to be tested for arsenic is conveniently first digested at a gentle heat with pure, 25 per cent. hydrochloric acid and some potassium chlorate, and the solution so obtained run into a simple Marsh apparatus (*cf.* Bronze Analysis, p. 212), in which hydrogen is being evolved from pure zinc. The hydrogen is ignited and a porcelain plate held in the flame. The dark brown shiny arsenic spots disappear immediately on addition of a drop of sodium hypochlorite. In order to distinguish them from antimony spots, G. Denigés<sup>1</sup> dissolves them in a few drops of nitric acid, warms the solution, and then adds four to five drops of a specially prepared molybdenum solution. In the presence of 0.01 to 0.02 mg. of arsenic, some yellow ammonium-arsen-molybdate is immediately formed, the regular crystals of which possess a characteristic appearance under the microscope. They are best examined in a polarisation microscope with crossed Nicols.

If pure iron (electrolytic, or reduced by hydrogen from absolutely pure ferric oxide) is introduced into a hydrochloric acid solution of antimony and arsenic, only arseniuretted hydrogen is evolved; the antimony is quantitatively separated as metal, together with a considerable quantity of arsenic. J. Thiele<sup>2</sup> makes use of this fact for the detection of small quantities of arsenic in presence of much antimony. Whilst 0.1 to 0.15 mg. of arsenic may be detected in an arsenic solution by means of the hydride evolved by the introduction of pure iron, the test becomes much more delicate if 2 to 3 c.c. of a concentrated solution of antimony oxychloride in hydrochloric acid of sp. gr. 1.124 are gradually run in. This procedure appears specially suited to the qualitative detection of arsenic in antimonial pharmaceutical preparations.

In Sweden it has been agreed<sup>3</sup> to examine tapestry, blinds, etc., printed

<sup>1</sup> *Comptes rend.*, 1890, **111**, 824; *J. Chem. Soc. Abstr.*, 1891, **60**, 364.

<sup>2</sup> *Annalen*, 1891, **263**, 361; *J. Soc. Chem. Ind.*, 1891, **10**, 857.

<sup>3</sup> *Z. anal. Chem.*, 1895, **34**, 88.

or painted with water-colours, by taking 200 sq. cm. of the material under examination, cutting it up, placing it in a 300 c.c. flask, adding 2 g. of ferrous sulphate free from arsenic, pouring on 50 to 80 c.c. of pure hydrochloric acid (sp. gr. 1.18 to 1.19), and distilling off the arsenic as chloride. The arsenic trisulphide obtained from the distillate is dissolved in dilute ammonia, the solution evaporated with 0.02 g. sodium carbonate on a clock-glass, the residue ground up with 0.3 g. of a mixture of sodium carbonate and potassium cyanide, the mixture brought into a bulb-tube (diameter of bulb 2 cm.), the arsenic volatilised by heating the bulb in a current of carbon dioxide, and condensed as a mirror in a small tube (1.5 to 2 mm. wide) joined on to the bulb. If a partially opaque arsenic mirror is obtained, the goods under examination are not allowed by the Swedish law to be sent on to the market.

## ANTIMONY

The metal (regulus), the liquated sulphide,  $\text{Sb}_2\text{S}_3$ , and the numerous antimonial preparations are generally prepared from *Stibnite* (grey antimony ore,  $\text{Sb}_2\text{S}_3$ ), the most frequently occurring ore of antimony, which contains 71.7 per cent. of antimony. Other antimony ores are:—*Antimony bloom* (Valentinite and Senarmontite),  $\text{Sb}_2\text{O}_3$ , and *Antimony ochre* (Cervantite,  $\text{Sb}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_5$ , and Stiblithe,  $\text{Sb}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_5 + 2\text{H}_2\text{O}$ ). Hard lead (antimonial lead) is prepared in large quantities in metallurgical works from lead and copper ores containing antimony; it comes on to the market with very varying contents of antimony (up to 30 per cent.).

The following products occur most frequently for analysis:—Ores, metallic antimony, hard lead, and other alloys rich in antimony (white metal, etc.). The dry assays for ores<sup>1</sup> are very inaccurate, but are still much employed in metallurgical works as working tests. Of the gravimetric methods of determination, the determination of the antimony as tetroxide and the electrolytic separation of the metal from solutions of the sulpho-salt are to be recommended; there are also several volumetric methods suited to technical purposes.

### A. METHODS OF ESTIMATION

**1. Estimation as Antimony Tetroxide,  $\text{Sb}_2\text{O}_4$  (Antimonious Acid).**  
—The antimony sulphide obtained by precipitation with sulphuretted hydrogen, or by acidifying solutions of the sulpho-salt, is conveniently treated with strong nitric acid until all the sulphur is oxidised,<sup>2</sup> the excess of acid removed by evaporation, the sulphuric acid carefully

<sup>1</sup> Cf. Kerl, *Probierbuch*, 2nd ed., 1894.

<sup>2</sup> Rössing, *Z. anal. Chem.*, 1902, **41**, 9; *J. Chem. Soc. Abstr.*, 1902, **82**, 230.

driven off, and the residue strongly ignited in an uncovered porcelain crucible supported in a round hole in a stout piece of asbestos board, and finally weighed as tetroxide.  $\text{Sb}_2\text{O}_4 \times 0.7898 = \text{Sb}$ .

A few milligrams of antimony sulphide are dissolved in warm ammonium sulphide, the solution evaporated in a large, weighed porcelain crucible, and the residue then oxidised with strong nitric acid. Larger quantities of precipitated antimony sulphide and sulphur are washed from the filter paper into a large dish, evaporated to dryness on the water-bath, the dish covered, and the contents completely oxidised with strong nitric acid; all the sulphur is thus immediately oxidised. After warming a short time, the contents of the dish are washed into a weighed crucible, and evaporated, etc., as above. (See also analysis of White-metal, p. 258.)

**2. Electrolytic Estimation**<sup>1</sup> (*cf.* Analysis of Hard Lead, p. 234).—According to Classen, the deposition of the antimony is best carried out in a solution of the sulphide in a large excess of concentrated sodium sulphide solution; with a solution containing from 50 to 70 per cent. of a cold, saturated sodium sulphide solution, the current used is from 1 to 2 ampères, and the E.M.F. may vary between 1.5 and 3 volts. By warming the solution to 60° to 80°, the deposition (in a sand-blasted dish) is hastened, so that 0.3 to 0.4 g. of antimony are completely separated in from one and a half to two hours. If the deposition is carried out in the warm solution, the dish must be washed without breaking the current. In the usual course of the analysis of ores, etc., by fusion with sodium carbonate and sulphur, or by treatment of the sulphuretted hydrogen precipitate with solution of sodium or potassium sulphides, antimony solutions are obtained which may be directly electrolysed after first decomposing the polysulphides by the careful addition of hydrogen peroxide, and then adding a considerable quantity of a cold, saturated solution of pure sodium sulphide. Arsenic is previously removed from the sulphuretted hydrogen precipitate by extraction with a saturated solution of ammonium carbonate, whilst tin may be present and is not deposited from a concentrated solution of the sulpho-salts.<sup>2</sup> After the deposition of the antimony, the tin may be precipitated as sulphide from the diluted solution by acidifying with sulphuric acid, and then converted into stannic oxide and weighed as such.

**3. Titration of the Antimony Oxide with Iodine** (F. Mohr).—The oxidation takes place in a slightly alkaline solution, according to the equation:—



<sup>1</sup> Cf. *Quantitative Analysis by Electrolysis*, A. Classen. English translation by B. Boltwood, 1903, p. 208; also, *Electro-Analysis*, E. F. Smith, 1908, p. 171.

<sup>2</sup> Cf. A. Fischer, *Z. anorg. Chem.*, 1904, 42, 363; *J. Soc. Chem. Ind.*, 1905, 24, 153.



According to Fresenius, a solution containing about 0.1 g. of antimony oxide, prepared by addition of water and tartaric acid, is neutralised with sodium carbonate, 20 c.c. of a cold, saturated solution of sodium bicarbonate and some starch solution added, and then titrated to the blue coloration with a standard iodine solution. Finkener adds a slight excess of the iodine solution, and titrates back, till the blue coloration just disappears, with a solution of sodium thio-sulphate checked against the iodine solution. One g. I = 0.5861 g.  $\text{Sb}_2\text{O}_3$ , or = 0.4735 g. Sb.

**4. Titration of the Antimony Oxide and of the Antimonic Acid** (F. A. Gooch and H. W. Gruener<sup>1</sup>).—The antimony oxide is titrated as above with an iodine solution standardised against a solution of tartar emetic. In a separate portion of the solution, after acidifying with some sulphuric acid, the antimonic acid is reduced by means of hydriodic acid (boiling the solution with potassium iodide), the solution decolorised by the careful addition of a dilute sulphurous acid solution, cooled, neutralised, etc., and the total content of antimony thus obtained.

**5. Titration of the Iodine liberated by the action of Antimonic Chloride on Potassium Iodide in Hydrochloric Acid Solution** (Parry<sup>2</sup>).—This method is suitable for alloys of lead, tin, and antimony. Copper, arsenic, and iron, if present, are included with the antimony in the determination, and must be separately estimated and allowed for. One to two grams of the finely divided alloy are dissolved in hydrochloric acid, potassium chlorate solution being added towards the end to assist solution. An excess of potassium chlorate is then added, the solution diluted, and the chlorine boiled off; after allowing to cool, the flask is filled with carbon dioxide from a Kipp apparatus, 20 c.c. of a 20 per cent. potassium iodide solution added, and the solution titrated rapidly with stannous chloride.

The allowance for arsenic, copper, and iron is as follows:—

1 per cent. As	=	1.6	per cent. Sb.
1 „ Cu	=	0.945	„
1 „ Fe	=	1.07	„

Giraud<sup>3</sup> adds carbon bisulphide to take up the liberated iodine, and titrates with sodium thiosulphate.

**6. Titration of Antimony Oxide with Potassium Bromate** (*cf.* Hard Lead, p. 235).

**7. Titration of the Sulphuretted Hydrogen evolved from Antimony Sulphide** (R. Schneider<sup>4</sup>).—Antimony trisulphide and pentasulphide

<sup>1</sup> *Amer. J. Science*, 1891, [3], 42, 213; *J. Chem. Soc. Abstr.*, 1892, 62, 242.

<sup>2</sup> *Assay of Tin and Antimony*, p. 39.

<sup>3</sup> *Bull. Soc. Chim.*, 1887, 46, 504; *J. Chem. Soc. Abstr.*, 1887, 52, 400.

<sup>4</sup> *Pogg. Ann.*, 1860, 110, 634.

liberate sulphuretted hydrogen on boiling with hydrochloric acid ; at the same time sulphur is separated from the pentasulphide. If the evolved sulphuretted hydrogen is led into a measured excess of iodine solution, considerably diluted with water, contained in a large retort, sulphur separates according to the equation :—



and the excess of iodine can be titrated back with a sodium thiosulphate solution checked against the iodine solution. The starch solution is not added in this case until the solution is of a wine-yellow colour.  $\text{Sb}_2\text{S}_3$  evolves  $3\text{H}_2\text{S}$ , which requires  $6\text{I}$  for oxidation. One gram  $\text{I}$  used, therefore, corresponds to  $0.3157$  g.  $\text{Sb}$ .

The determination is carried out as follows :—The filter paper containing the antimony sulphide (which may be admixed with arsenic sulphide) is introduced into a wide-necked flask, and 25 per cent. hydrochloric acid allowed to run in through a safety funnel. The long delivery tube is inserted into the body of the retort, which is inverted, filled with dilute iodine solution, and rests on a wicker stand. The flask is heated and the liquid allowed to boil for ten minutes ; the delivery tube is withdrawn from the iodine solution during the boiling. The receiver (retort) is then cooled under the tap, the iodine solution washed into a large beaker, and the excess of iodine titrated back. As a check, the antimony solution in the flask may be titrated by Mohr's method (No. 3, p. 282), after the addition of tartaric acid, diluting, and filtering. Since the antimony sulphide precipitate generally contains chlorine, this method does not give absolutely accurate results, but may, nevertheless, be employed for technical determinations.

## B. SEPARATION OF ANTIMONY, ARSENIC, AND TIN

The best methods of separation have already been described under the analysis of Hard Lead, p. 234, and of White-metal, p. 258. Arsenic and antimony are separated by diluting the solution of the sulphides in hydrochloric acid and potassium chlorate after the addition of tartaric acid, filtering, saturating with ammonia, and precipitating the arsenic acid with magnesia mixture, etc. A small quantity of arsenic may be extracted from the mixed sulphides by means of a saturated solution of ammonium carbonate. Tin and antimony are best separated by means of iron, the metallic antimony being redissolved and deposited electrolytically as metal from a solution of the sulpho-salt (*cf.* Method 2, p. 282), and the tin precipitated as sulphide from the antimony-free solution, etc. If arsenic and tin are present together with antimony, it is best to precipitate the arsenic as pentasulphide by passing

sulphuretted hydrogen into the cold, strong hydrochloric acid solution, to filter through an asbestos filter, oxidise the filtrate with a slight excess of bromine water, dilute somewhat, and precipitate the antimony by means of pure iron, etc.

Hampe<sup>1</sup> uses the following method of separation:—After adding a fair quantity of tartaric acid to the solution and precipitating the arsenic as magnesium ammonium arsenate, the filtrate is acidified, sulphuretted hydrogen passed in, the tin and antimony sulphides dissolved in freshly prepared sodium sulphide solution, and the concentrated, cold solution of the sulpho-salts oxidised by the addition of small quantities of sodium peroxide until a fresh addition causes effervescence with evolution of oxygen. To bring about complete separation of the sodium pyroantimoniate, after boiling and cooling, one-third of the volume of alcohol of sp. gr. 0.833 is added, and the precipitate filtered off after standing for twenty-four hours. Rose recommends washing the precipitate first with a mixture of equal volumes of water and alcohol (sp. gr. 0.83), and then with a mixture of one volume of water and three volumes of alcohol; a few drops of sodium carbonate solution should be added to the liquids used in the washing. The sodium pyroantimoniate is dissolved in hydrochloric acid containing tartaric acid, and the antimony precipitated by sulphuretted hydrogen and finally weighed as oxide. The alcohol is driven off from the filtrate from the sodium pyroantimoniate, the solution acidified with hydrochloric acid, sulphuretted hydrogen passed in, and the precipitate of tin sulphide converted by careful ignition into oxide, which is finally strongly ignited after the addition of a small piece of ammonium carbonate.

### C. SPECIAL METHODS OF ANALYSIS

#### I. For Ores, Liquated Stibnite, and Slags.

(a) One-half to one gram of the finely ground substance is fused in a covered porcelain crucible with six times its weight of a mixture of equal parts of sodium carbonate and sulphur (or six times the weight of sodium thiosulphate dehydrated at 210°) until no more sulphur is evolved. The cold melt is extracted with 40 to 50 c.c. of hot water, the solution filtered into a matted Classen dish, concentrated by evaporation on the water-bath, the polysulphides decomposed by the careful addition of hydrogen or sodium peroxide, the volume of the solution made up to 150 c.c. after the addition of 60 to 70 c.c. of a cold, saturated solution of sodium sulphide, and then electrolysed hot (*cf.* Method 2, p. 282). If the substance contains arsenic in considerable quantity, the sulpho-salts in the aqueous extract of the fusion are completely oxidised by repeated additions of small quantities of sodium peroxide (arsenic is

<sup>1</sup> *Chem. Zeit.*, 1894, 18, 1900; *J. Soc. Chem. Ind.*, 1895, 14, 302.



thereby converted into sodium arsenate), the solution digested with the larger quantity of cold, saturated sodium sulphide solution until all the sodium pyroantimoniate is completely dissolved, and then electrolysed; by this means arsenic acid is not reduced. The antimony is removed from the dish by alternately warming with strong nitric acid and hot potassium hydroxide, or with nitric and tartaric acids.

If electrolytic apparatus is not available, the solution of the sulphosalts from the fusion is warmed with excess of dilute sulphuric acid, the sulphides filtered off, the antimony separated if necessary from arsenic and tin, and determined finally as oxide (Method I, p. 281).

Oxidised ores, difficultly soluble in acids, are likewise treated by fusion with sodium carbonate and sulphur, etc. Carnot's method, which consists in the conversion of the oxides into antimony sulphide by heating for a long time at  $300^{\circ}$  in an atmosphere of dry sulphuretted hydrogen, is of no practical value. (Cf. also Estimation of Antimony in Arsenic Ores, p. 278.)

(b) The finely ground ore or liquated stibnite is dissolved in aqua regia, or in hydrochloric acid and potassium chlorate, the solution made alkaline with potassium hydroxide, sodium sulphide solution added, warmed until all sodium pyroantimoniate has dissolved, filtered, and after adding a large quantity of sodium sulphide solution, the solution is electrolysed with a current of 2 ampères. Arsenic is not deposited, since it is present as arsenic acid. The usual analytical method may of course also be applied in this case.

(c) *Estimation of Sulphur*.—Several decigrams of the ore are heated in a current of chlorine, tartaric and hydrochloric acids added to the liquid in the receiver, the free chlorine expelled from the solution by warming and passing in carbon dioxide, antimony, arsenic, and tin precipitated by sulphuretted hydrogen (Finkener), the sulphides filtered off, the sulphuretted hydrogen in the filtrate boiled off, and the sulphuric acid precipitated as usual with barium chloride solution.

## 2. For Metallic Antimony (Regulus Antimonii).

Commercial antimony generally contains lead, silver, arsenic, copper, iron, and a little sulphur as impurities; bismuth, nickel, and cobalt may be present. The pure metal has a silver-white colour, whilst antimony containing lead is more or less of a bluish white colour with a fracture less coarsely crystalline than that of the pure metal. In commerce, the so-called antimony star<sup>1</sup> on the top of the ingot or cake is taken as a special sign of purity; this is only formed on the pure metal, however, if it solidifies under a covering of slag and is protected against shock.

<sup>1</sup> A specimen of antimony from Hungary possessing this star-like surface contained the following impurities:—Arsenic, 0.330 per cent.; iron, 0.052 per cent.; and sulphur, 0.720 per cent. (Schnabel).

For the analysis, several grams of the finely pulverised metal are dissolved in nitric and tartaric acids, the solution saturated with ammonia, copper, lead, and iron precipitated by the careful addition of sulphuretted hydrogen (Finkener's method, p. 258), the sulphides filtered off, and the metals determined in the usual way. For the estimation of the arsenic a separate weighing of several grams is dissolved in hydrochloric acid and potassium chlorate, the chlorine driven off by gently warming, the solution cooled, a large quantity of concentrated hydrochloric acid added, sulphuretted hydrogen passed in for a long time, arsenic and copper precipitated as sulphides and filtered off through an asbestos filter (*cf.* Analysis of White-metal, p. 259). The arsenic sulphide is extracted with ammonium carbonate solution, the solution evaporated, oxidised with strong nitric acid, and the arsenic acid precipitated in the usual way with magnesia mixture, leaving the copper in the ammoniacal solution.

The determination of sulphur is carried out as described under (c) (p. 286).

### 3. For Antimony Alloys.

The methods of analysis have already been described under the analysis of Hard Lead (p. 233), and of White-metal (p. 258).

### 4. For Antimonial Preparations and Colours.

(Oxides, Tartar Emetic, Gold Sulphur, Antimony Cinnabar, etc.)

These are either dissolved or fused with sodium carbonate and sulphur, and their content of antimony determined by Methods 1 to 6 (p. 281).

## ZINC

The products that occur for technical examination are:—Raw and calcined ores and waste from the dressing of the ores, commercial zinc, zinc dust, hard zinc or bottom zinc from the galvanising of iron, zinc dross and ashes, materials from the metallurgical treatment of lead, copper, and iron ores containing zinc, zinc-white residues, and fumes. In addition, especially in zinc works proper, crude or work zinc has to be analysed as well as the residues from the distillation of zinc.

The most important ores of zinc are:—

*Zinc blende* or *Blende*,  $\text{ZnS}$ , contains in its purest state 67 per cent. of zinc, but invariably contains iron (up to 18 per cent.) as impurity, and traces of cadmium up to 3 per cent. Many black blendes contain manganese and traces of tin, less frequently traces of indium and gallium also. Pyrites, galena, copper pyrites, arsenic, and antimony ores are frequently found with blende.

*Calamine*,  $\text{ZnCO}_3$ , containing 52 per cent. of zinc; a part of the zinc

in the carbonate is usually replaced by iron, manganese, cadmium, calcium, and magnesium. The green calamine of Laurion is coloured with copper carbonate; rich deposits of calamine have also been found there in antique aqueducts. Common calamine, with less than 30 per cent. of zinc and mixed with clay, ferric hydroxide, manganese oxide, limestone, and dolomite, is much more frequent.

*Crystallised Silicate of Zinc*,  $\text{Zn}_2\text{SiO}_4 + \text{H}_2\text{O}$ , contains 53.7 per cent. of zinc, and is known as "electric calamine" when associated with the frequently occurring earths, clays, etc., as impurities.

*Willemite*,  $\text{Zn}_2\text{SiO}_4$ , containing 58.1 per cent. of zinc, and *Troostite*,  $2(\text{Zn}, \text{Mn})\text{O}, \text{SiO}_2$ , as well as *Red Zinc Ore* (zinc oxide with up to 12 per cent. of manganese as oxide) and *Franklinite*,  $3(\text{FeZn})\text{O} + (\text{FeMn})_2\text{O}_3$ , are found in large quantities exclusively in the state of New Jersey.

### A. METHODS OF ESTIMATION

Sufficiently accurate methods of dry assay are not known. In technical work the zinc in ores, etc. (with the exception of alloys of zinc with copper, nickel, etc.), is determined, by preference, volumetrically, either by the titration of the ammoniacal solution with sodium sulphide (Schaffner's method), or by the potassium ferrocyanide method; the latter method is generally employed in England and in the United States, the former method in Germany. The gravimetric determination of the zinc as zinc sulphide (Schneider and Finkener's method) is rarely used in commercial work, and then only as a deciding test; it is the most accurate of all methods of estimation. Up to the present, none of the many electrolytic methods proposed have found application to the determination of zinc in ores, on account of the necessity of previously separating the other metals and of the lengthy manipulation involved.

**1. Estimation of the Zinc as Sulphide,  $\text{ZnS}$ .**—This method permits of a simple and complete separation of zinc from the metals (iron, manganese, nickel, cobalt) which are not precipitated from a dilute mineral acid solution by sulphuretted hydrogen, and is best carried out in a very dilute solution rendered just acid with sulphuric acid. One-half to one gram of the dried finely ground substance (raw or calcined ore, residues, ashes, etc.) are dissolved in a flask in hot aqua regia (from concentrated acids), or by heating with nitric acid saturated with potassium chlorate. Excess of previously diluted sulphuric acid is added, and the contents of the flask boiled until dense fumes of sulphuric acid are evolved. The syrupy residue is taken up with water (50 c.c.), sulphuretted hydrogen passed in, the precipitate (copper sulphide, cadmium sulphide, lead sulphate, gangue, etc.) filtered off, and washed with diluted sulphuretted hydrogen water acidified with



sulphuric acid. The filtrate is boiled to expel the sulphuretted hydrogen, cooled, and neutralised, after the addition of a piece of Congo red paper, with ammonia until the paper just turns a pale violet colour. Any cloudiness due to ferric hydroxide, etc., is removed by the addition of a few drops of normal sulphuric acid; if the liquid becomes strongly heated (on account of its being strongly acid), after nearly neutralising, it is cooled by placing it in cold water, and then the cooled solution further neutralised. Litmus paper cannot be used, since neutral solutions of zinc sulphate and of zinc chloride show an acid reaction with litmus. The solution is diluted according to the amount of zinc it contains, so that 100 c.c. do not contain more than 0.1 g. of zinc. The beaker is then covered with a clock-glass and a continuous current of sulphuretted hydrogen passed in for one and a half to two hours through a bent delivery tube with a fine opening. If the precipitation of the white zinc sulphide does not begin for a quarter of an hour or more, the solution contains too much free acid; this will be recognised later by considerable amounts of zinc sulphide adhering fairly fast to the sides of the beaker. After standing twelve to eighteen hours, the solution is filtered through a strong, ash-free paper, the zinc sulphide brought on to the paper and washed with water (200 to 300 c.c.) in which about 5 g. of ammonium sulphate are dissolved, after the addition of some sulphuretted hydrogen water. A slight opalescent cloudiness of the filtrate, which generally does not take place till after the filtration, is due to very finely divided sulphur, which is separated by the action of the oxygen in the air on the sulphuretted hydrogen. Before bringing the precipitate on to the filter paper, another beaker is placed under the long-necked filter funnel, and the first runnings of the cloudy filtrate poured back until the pores of the filter paper become stopped up and the filtrate runs through perfectly clear. The filter paper with the precipitate is then dried in an air-bath, the zinc sulphide removed as completely as possible on to glazed paper, the paper ignited in a Rose crucible, previously weighed with the lid (the ignition requires about one hour), the zinc sulphide, together with an equal volume of powdered roll sulphur, introduced into the cooled crucible, the lid placed on, and pure dry hydrogen led in by means of the porcelain delivery tube. After all the air is driven out, the crucible is heated with a Bunsen burner with a small flame; when all the sulphur has escaped, the temperature is increased to a bright red heat, and after strongly igniting for twenty minutes, the crucible is allowed to cool in the current of hydrogen.

$$\text{ZnS} \times 0.6709 = \text{Zn}.$$

Care must be taken to rub off as little of the fluff as possible from the filter paper when removing the precipitate, otherwise carbon will be found with the weighed zinc sulphide. The filtrate from the zinc

sulphide is evaporated in a large porcelain dish over a free flame to about 200 c.c., after cooling, neutralised with ammonia, using Congo red paper as indicator, very slightly acidified with a little normal sulphuric acid, and then sulphuretted hydrogen passed in for an hour. If any zinc sulphide separates after standing for some time, it is filtered off and treated as above. The precipitation in a very dilute hydrochloric acid solution is not to be recommended, because on ignition in hydrogen a loss of zinc as zinc chloride may take place owing to a small amount of ammonium chloride being retained in the dry zinc sulphide. A yellow deposit on the underneath side of the crucible lid is cadmium sulphide; this is generally to be found in determining zinc in brass or German silver, when the copper is determined electrolytically, and the solution from the copper neutralised, diluted, and the zinc precipitated with sulphuretted hydrogen. The deposit is weighed together with the zinc sulphide as such, since the separation or quantitative estimation of the very small quantity of cadmium is quite superfluous.

In the analysis of German silver (*cf.* Nickel, p. 319) several cubic centimetres of distilled sulphuric acid are added to the filtrate from the zinc sulphide before evaporating, otherwise nickel sulphide easily separates and adheres firmly to the sides of the dish. On subsequent neutralisation of the solution with ammonia, a corresponding quantity of ammonium sulphate is formed, the presence of which is an advantage in the electrolytic deposition of the nickel.

**2. The Electrolytic Estimation of Zinc** is of but little practical importance, since good adhesive deposits of the metal are only obtained by very slow deposition, and it is essential to work with nearly pure zinc solutions. According to Classen, good results are obtained, for example, if a sulphuric acid solution containing several decigrams of zinc is neutralised with potassium hydroxide, 4 to 5 g. of neutral potassium oxalate added, warmed to dissolve any precipitated zinc oxalate, 4 to 5 g. of potassium sulphate dissolved in the solution (about 100 c.c.), which is then cooled and electrolysed, first with a current of 0.25 to 0.5 ampère, and finally with 1 ampère. The zinc is not deposited directly on to the platinum electrode (cone or dish), but this latter is first coated with a clean electrolytic deposit of copper or silver, since zinc deposited directly on to platinum when dissolved off the electrode by means of acids leaves behind peculiar dark spots (an alloy with platinum appears to be formed), and the electrode after repeated ignition and treatment with hydrochloric acid does not keep a constant weight. For coating the dish with copper, a copper sulphate solution acidified with nitric acid or a potassium copper cyanide solution is used; and for silvering, the usual silvering solution of potassium silver cyanide, containing 4 to 10 g. of silver and 10 to 25 g. of potassium cyanide per litre. It is more practical to use dishes of fine silver; in the technical

laboratories at Eisleben the zinc is deposited on copper cylinders. A method recommended by H. Paweck<sup>1</sup> consists in depositing the metal on amalgamated brass wire gauze, and is comparatively quick. When using a silvered or coppered cone or dish, the end of the deposition is determined either by adding about 20 c.c. of a cold, saturated potassium sulphate solution and electrolysing for another hour, or by taking out a few cubic centimetres by means of a pipette and warming with ammonium sulphide. The washing is done without breaking the circuit, and the cone dipped into water, then into absolute alcohol, and dried quickly over a heated dish. Small quantities of iron are deposited as metal along with the zinc; the zinc containing iron is dissolved off the silvered or silver electrode in warm dilute sulphuric acid, the solution cooled, the iron titrated with potassium permanganate and deducted as iron.

E. F. Smith<sup>2</sup> states that zinc is especially readily determined by means of a rotating anode and mercury cathode; he uses a zinc sulphate solution containing free sulphuric acid.

The numerous other methods proposed for the electrolytic estimation of zinc are described in the literature on electrolytic analysis.<sup>3</sup>

**3. Volumetric Estimation of Zinc.**<sup>4</sup>—(a) *Schaffner's Method* (cf. Vol. I., p. 289).—This consists in the precipitation of the zinc in an ammoniacal solution as zinc sulphide by means of a sodium sulphide solution, which is added until a slight excess is recognised by means of an indicator. Iron, copper, lead, cadmium, manganese, nickel, and cobalt interfere with the accuracy of the method, and must previously be removed; the two latter hardly ever occur in appreciable quantities in ores of zinc. Sulphide ores (raw and calcined blends) and residues are dissolved in strong nitric acid, aqua regia, brom-hydrochloric acid, or in nitric acid and potassium chlorate, calamine in aqua regia; electric calamine is best dissolved in 50 per cent. sulphuric acid with addition of hydrofluoric acid (in a platinum dish), evaporated, and the iron oxidised with a little nitric acid. The metals precipitated by sulphuretted hydrogen (lead, copper, and cadmium) are removed by passing the gas into the moderately dilute solution; the filtrate is boiled, the ferrous salts oxidised by the addition of nitric acid or aqua regia, the solution much diluted, bromine water added, then saturated with ammonia and ammonium carbonate solution, and the iron and manganese precipitate filtered off. If the ore contains above 5 per cent. of iron, it is redissolved in dilute sulphuric acid, after washing the precipitate for a short time, bromine water (10 to 20 c.c.) added to the diluted solution, and the precipitation repeated, since the ferric

<sup>1</sup> *Chem. Zeit.*, 1898, **22**, 646; *J. Chem. Soc. Abstr.*, 1899, **76**, 250.

<sup>2</sup> *Electro-Analysis*, p. 120.

<sup>3</sup> Cf. p. 159.

<sup>4</sup> Cf. "Technical Assay of Zinc," Greenwood and Brislee, *J. Inst. Metals*, 1909, **2**, 249.



hydroxide precipitate carries down with it a considerable quantity of zinc hydroxide.

The precipitation may also be effected in a 500 c.c. graduated flask, which is filled to the mark after cooling, shaken round, and not taking into account the volume of the precipitated ferric hydroxide, several hundred cubic centimetres are filtered through a dry filter paper, and 100 c.c. taken for each titration; in this case it is well to prepare the solution of chemically pure zinc which is going to be used as standard in a similar graduated flask, and to add approximately the same amount of iron (as ferric chloride solution), to dilute, add excess of ammonia and ammonium carbonate, make up to 500 c.c., etc. The amount of zinc retained by the ferric hydroxide precipitate is then approximately the same in both cases. This method is quicker than the above.

The excess of ammonia in the solutions to be titrated must be slight; it is usual to allow solutions withdrawn by the pipette to stand uncovered overnight. The sodium sulphide solution is prepared from a cold, saturated solution of pure crystallised sodium sulphide by diluting with ten to twenty times the volume of distilled water and connecting up from a large stock bottle permanently with a burette. The best indicator for the end-point is "Polka paper," a paper sized and covered with white lead; it is prepared for the use of zinc metallurgical laboratories. The titration is carried out in strong beakers (battery glasses) and the solution stirred with a glass rod, which serves for the removal of drops of liquid from time to time which are allowed to drop on to the test paper. A modification of the method of titration consists in adding a flake of freshly precipitated ferric hydroxide to the solution contained in a flask, keeping the solution rapidly rotating during the addition of the sodium sulphide solution and continuing until the flake is blackened. The flask is frequently held over a plate-glass mirror to facilitate the observation of the flakes. The method is sufficiently accurate for all technical purposes.

(b) *Galletti's Potassium Ferrocyanide Method*, modified by Fahlberg,<sup>1</sup> v. Schulz, Low,<sup>2</sup> and others, consists in precipitating the zinc by means of a solution of potassium ferrocyanide in a solution warmed to 60° to 80°, acidified with hydrochloric acid, and free from iron, manganese, copper, lead, and cadmium, the end-point being recognised by a spot test, using a solution of uranium acetate as indicator.

This method is generally used in preference to the sodium sulphide method, both in England and in America, as it has the advantage of the greater stability of the solution used for the titration.

The method of solution for the ore and the separation of the interfering

<sup>1</sup> Fresenius, *Quantitative Analysis*, 7th ed., vol. ii., p. 283.

<sup>2</sup> *Berg. u. Hütten. Zeit.*, 1893, 52, 338.

metals may be carried out as described under Schaffner's method. The alkaline solution thus obtained is neutralised with hydrochloric acid, an excess of 5 c.c. added, the solution made up to 250 c.c. with hot water, and titrated. The solution of potassium ferrocyanide contains 22 g. of the crystallised salt to the litre; a 5 per cent. solution of uranium acetate is used as indicator. Uranium nitrate or ammonium molybdate may also be used as indicators.<sup>1</sup>

The titration in an ammoniacal tartrate solution (see Special Methods, Voigt, p. 294) is sometimes used.

## B. SPECIAL METHODS OF ANALYSIS

### 1. For Ores, Calcined Ores, Ashes, Residues, etc.

*Loss on Ignition.*—A few grams of calamine or electric calamine are weighed in a porcelain crucible, gradually heated up to strong ignition, and the loss in weight (carbon dioxide and water) determined after cooling.

*Sulphur* (*cf.* Vol. I., p. 289).

In the working of the calciners, the roasted blends are tested to see if sufficiently calcined (F. Meyer) by gently warming a measured quantity of the fine powder in a small flask with 10 c.c. of hydrochloric acid (1 : 2), at the same time holding a strip of filter paper moistened with a dilute alkaline solution of lead acetate in the neck of the flask. The degree of calcination is judged from the intensity of the coloration produced on the paper.

*Zinc.*—This is generally determined volumetrically. In the case of differences of 1 per cent. and over in the results obtained, the gravimetric estimation as zinc sulphide (p. 288) is used as a deciding test.

*Gravimetric Estimation of Zinc* (G. Schlegel).<sup>2</sup>—Two grams of the finely ground and sieved ore, dried at 100°, are dissolved in a tall beaker in 20 c.c. of strong aqua regia, the silica separated by evaporating the solution to complete dryness, the residue again taken down with a little hydrochloric acid, digested with 15 c.c. of hydrochloric acid, and boiled with 200 c.c. of water. Without filtering, excess of ammonia is added to the solution, which is repeatedly shaken round and then allowed to stand for ten minutes until the hydroxides of iron, aluminium, and lead have settled. If manganese is present, a few drops of hydrogen peroxide or a very little sodium peroxide are added before adding the ammonia. The precipitate is filtered on to a smooth filter paper 15 cm. in diameter, washed somewhat, then again dissolved

<sup>1</sup> Nissenson and Kettembeil, *Chem. Zeit.*, 1905, 27, 591.

<sup>2</sup> Private communication to Prof. Pufahl. This method is usually employed at the Hohenlohe Works, Upper Silesia.

in hydrochloric acid in the first beaker, after diluting to 200 c.c., again precipitated with ammonia (after addition of hydrogen peroxide, if necessary), filtered, and this manipulation repeated a third time. The combined filtrate is placed in a litre flask, cooled, and after diluting up to the mark, 200 c.c. (corresponding to 0.4 g. of substance) are usually withdrawn with a pipette. In the case of ores containing less than 15 per cent. of zinc, 400 c.c. are taken, if less than 10 per cent., 600 c.c., and in the case of those containing over 55 per cent., only 100 to 150 c.c. are taken for the precipitation with sulphuretted hydrogen. The solution is warmed in an Erlenmeyer flask, a rapid current of sulphuretted hydrogen passed in for ten minutes, then acidified with acetic acid, again gently warmed, and the precipitate filtered on to a weighed Gooch crucible, using suction.

The Gooch crucible is prepared as follows:—The filter disc is removed, the crucible firmly inserted in the rubber ring, fitted on to the filter flask, and the suction pump started. The crucible is then one-third filled with water containing fine fibrous asbestos in suspension (the asbestos having been previously boiled in dilute hydrochloric acid). The layer of asbestos is pressed down firmly with the finger, especially at the edges, until the noise of the air sucking through is no longer perceptible. The filter disc is then laid on, the crucible dried slowly, ignited over a spirit lamp, and weighed when quite cold (*cf.* Vol. I., p. 25).

Special care should be taken in the filtration to first filter the liquid above the precipitate, and then to bring the zinc sulphide into the crucible at one operation; otherwise the pores become clogged and the filtration is considerably interfered with. After the liquid has been completely transferred the precipitate is washed seven to eight times with dilute sulphuretted hydrogen water, by filling the crucible up to the edge, allowing to drain, and filling up again, and so on. The crucible is then lifted out, cleaned externally, thoroughly dried, a little powdered sulphur added, and then ignited in a current of hydrogen.

$$\text{ZnS} \times 0.6709 = \text{Zn}.$$

In case the ore contains copper, cadmium, or arsenic, in weighable quantities, these are removed in the original hydrochloric acid solution by means of sulphuretted hydrogen, the sulphuretted hydrogen and ferrous chloride in the filtrate oxidised, and then ammonia added. If over 10 per cent. of lead is present, or less lead together with relatively little iron, it is separated by evaporating the solution with sulphuric acid, etc., otherwise some lead will be found in the ammoniacal zinc solution.

*Volumetric Estimation of Zinc (Voigt).*—Forty-six grams of pure crystallised potassium ferrocyanide are dissolved and the solution made up to 1 litre. For standardising, 12.4476 g. of chemically pure zinc oxide are dissolved in hydrochloric acid, the solution diluted up to 1 litre, and stored in a well-stoppered bottle. One c.c. contains exactly



10 mg. of zinc. Ten c.c. are withdrawn with a pipette, 10 c.c. of a solution of tartaric acid (200 g. in 1 litre), 10 c.c. of a ferric chloride solution (60 g. in 1 litre), and 100 c.c. of water added, ammonia added in slight excess, and the solution titrated with the solution of potassium ferrocyanide, until a permanent blue colour is produced on removing a drop and adding it to acetic acid (1 : 3) on a pitted porcelain plate. After carrying out the preliminary and control titrations, the solution of potassium ferrocyanide is diluted so that 1 c.c. corresponds accurately to 10 mg. of zinc.

For the estimation, 1 g. of the finely ground ore, dried at  $100^{\circ}$ , is warmed with 10 c.c. of fuming hydrochloric acid until all the sulphuretted hydrogen is completely driven off, 3 c.c. of fuming nitric acid are then added, and the solution considerably evaporated, but not quite to dryness. Ten c.c. of the solution of tartaric acid are then added, also 10 c.c. of the ferric chloride solution, if necessary, the solution made slightly ammoniacal, diluted with water to 100 to 120 c.c., and titrated as above.

*Lead and Iron.*—Five grams of the finely ground and sieved ore are dissolved in hydrochloric acid and fuming nitric acid, 10 c.c. of distilled sulphuric acid added, and the solution boiled till white sulphuric acid fumes are evolved. The cooled mass is moistened with 75 c.c. of water, and then boiled and cooled. The separated lead sulphate, together with the gangue, is filtered off, washed, and the filter paper with its contents digested in a beaker with a concentrated solution of sodium acetate or neutral ammonium acetate so as to dissolve the lead sulphate. The solution is then filtered through a smooth filter paper which is well washed with water containing acetate, the lead in the filtrate precipitated with potassium bichromate, and after settling, the precipitate filtered off on to a Gooch crucible and washed ten times with warm water. The crucible is then removed from the filter-flask, cleaned externally and dried, first in an air-bath, and finally over a spirit lamp at about  $200^{\circ}$ .  $\text{PbCrO}_4 \times 0.6408 = \text{Pb}$ .

The iron is determined in a twentieth part of the filtrate from the lead sulphate and gangue, by reducing with zinc (amalgamated small rods of zinc suspended in a basket of platinum) after the addition of sulphuric acid, testing with potassium thiocyanate, and titrating the cooled solution, acidified with sulphuric acid, with potassium permanganate.

## 2. For Metallic Zinc (*Crude Zinc, Spelter, and Zinc Dust*).

(a) *Crude Zinc.*—This invariably contains lead, some iron, cadmium, suspended carbon, and traces of sulphur as impurities; in addition, small quantities of tin, copper, silver, and arsenic are frequently present, traces of antimony and silicon being rarely found. Larger quantities of

silicon (several tenths per cent.) have up to the present only been found in a few kinds of North American zinc.

In smelting works only the lead and iron are usually determined. Five grams of the cut-up borings from several plates are warmed in a covered porcelain dish with 50 c.c. of dilute sulphuric acid (1 : 4), and after the evolution of hydrogen has ceased 1 c.c. of nitric acid (sp. gr. 1.2) is added. The solution is evaporated and heated on the sand-bath until sulphuric acid fumes are copiously evolved, after which the cooled residue is heated for some time on a boiling water-bath with 50 c.c. of water, the solution then cooled, the lead sulphate collected on a small filter paper, and determined in the usual way. To an aliquot part of the filtrate (100 c.c.), 5 c.c. of ordinary 25 per cent. hydrochloric acid is added, and sulphuretted hydrogen passed in; the cadmium sulphide thus precipitated may be determined as described below. For the estimation of the iron, 5 to 10 g. of the drillings are dissolved in hot, dilute sulphuric acid, the solution decanted off from undissolved lead, and the iron titrated in the cooled solution with potassium permanganate.

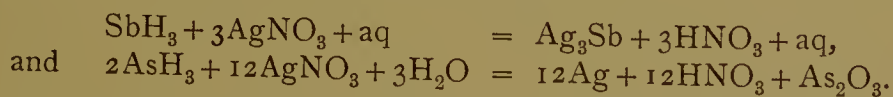
(b) *Commercial Zinc (Refined Zinc)*.—This contains the same impurities as crude zinc in smaller quantities. The following method of F. Mylius and O. Fromm<sup>1</sup> gives very good results:—Two hundred c.c. of water are poured over 100 g. of an average sample in a flask of about 2 litres capacity, and the amount of nitric acid necessary for solution added in several portions, finally heating. The solution is then cooled, an excess of ammonia added until all the zinc hydroxide is redissolved, diluted to about 2 litres, and very dilute ammonium sulphide solution added in small quantities, shaking the solution round during the addition, until the freshly-formed precipitate appears white, like pure zinc sulphide. On warming the solution to 80°, the precipitated zinc sulphide is quickly decomposed by the other metallic salts, so that all the lead, cadmium, copper, silver, and bismuth pass into the precipitate. When the solution has cleared, it is filtered; on adding ammonium sulphide to the filtrate, pure white zinc sulphide is precipitated perfectly free from lead, cadmium, etc. The precipitate is then dissolved off the filter paper in hot dilute hydrochloric acid, whereby any copper and silver present as sulphides remain undissolved, and may be separated and determined in the usual way. The hydrochloric acid solution is evaporated with excess of sulphuric acid to separate the lead, the residue taken up with water, some alcohol added, and the lead sulphate filtered off. The alcohol in the filtrate is removed by evaporation, the solution neutralised with ammonia, 10 c.c. of 25 per cent. hydrochloric acid (sp. gr. 1.125) added for every 100 c.c. of liquid, and the cadmium precipitated, free from zinc, as cadmium sulphide by passing in

<sup>1</sup> *Z. anal. Chem.*, 1897, 36, 37.

sulphuretted hydrogen for a long time. The precipitate is filtered off, dissolved in hot nitric acid (sp. gr. 1.2), the solution evaporated in a weighed porcelain crucible with a slight excess of sulphuric acid, the free sulphuric acid driven off, the residue gently ignited, and weighed as cadmium sulphate.  $\text{CdSO}_4 \times 0.5392 = \text{Cd}$ .

The sulphuretted hydrogen is expelled from the filtrate from the cadmium sulphide by boiling, the iron oxidised with bromine water, the solution saturated with ammonia, the ferric hydroxide filtered off, and dissolved in a little hydrochloric acid. This hydrochloric acid solution (which contains zinc) is diluted, saturated with ammonia, warmed, and the pure hydroxide obtained filtered off and finally weighed as ferric oxide.

Sulphur, arsenic, and antimony are determined by O. Günther's method.<sup>1</sup> One hundred grams of drillings obtained by completely boring through several plates, are placed in a large flask, the air in which is then completely driven out with a current of pure hydrogen, absolutely pure dilute sulphuric acid run in, and the evolved gas passed first through a wash-bottle containing cadmium potassium cyanide solution, and then through a second wash-bottle containing silver nitrate solution. When the evolution of hydrogen ceases, pure hydrogen is led into the flask for some time through the funnel tube which passes to the bottom of the flask and which is bent up at the end. In the first wash-bottle all the sulphur separates as cadmium sulphide, which is filtered off and converted into cadmium sulphate (see above) and weighed. In the second wash-bottle silver antimonide and metallic silver separate, whilst all the arsenic is in solution as silver arsenite. These decompositions take place in accordance with the equations:—



The precipitate (silver and silver antimonide) is filtered off, dissolved in nitric and tartaric acids, the silver precipitated as chloride with hydrochloric acid, the antimony in the filtrate precipitated (after diluting and nearly neutralising) with sulphuretted hydrogen, and finally determined as antimony tetroxide. The arsenic present may be calculated from the above equations, if from the total silver given by the weight of silver chloride, the silver present as combined with antimony, is deducted; then  $12\text{Ag} = 2\text{As}$ .

In case the zinc under examination should contain a high percentage of lead (1 to 3 per cent.), it is advisable to separate the antimony, perhaps also the arsenic, by ordinary gravimetric methods, since under such conditions the antimony is not completely evolved as hydride, on treatment with dilute sulphuric acid. The portion of the antimony in

<sup>1</sup> *Z. anal. Chem.*, 1881, 20, 503; *J. Soc. Chem. Ind.*, 1882, 1, 118.



combination with the zinc, appears to be evolved as hydride, whilst the remainder, in combination with the lead, remains behind with the residue of spongy lead.

If arsenic only is to be estimated, 10 g. or more of the sample are oxidised by the addition, from time to time, of strong nitric acid, the solution evaporated, and the evaporation repeated with considerable quantities of pure hydrochloric acid. The solution is transferred to a flask, pure fuming hydrochloric acid and ferrous sulphate added, and all the arsenic distilled off as arsenic chloride (p. 196). Prauss' method (*cf.* Arsenic, Special Methods, 6 p. 279) may also be employed, in which case the sample is dissolved in pure dilute sulphuric acid.

For the accurate determination of sulphur in zinc, it is advisable, according to Elliot and Storer, to dissolve the metal in hydrochloric acid prepared from a solution of pure calcium chloride and oxalic acid.

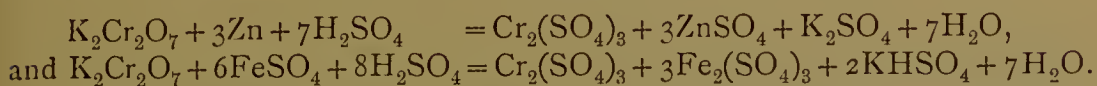
Tin is determined by digesting a large weighing of the sample with an insufficient quantity of dilute sulphuric acid to effect complete solution, decomposing the residue, after washing by decantation, with strong nitric acid, and boiling after addition of water and filtering off the stannic acid. In spelter made by melting up old zinc several tenths per cent. of tin (from the solder) are frequently found.

Silicon, which seldom occurs in spelter, is determined in the same way as in aluminium. A large weighing is dissolved in pure sodium hydroxide by warming in a platinum dish, the solution saturated with hydrochloric acid, evaporated to dryness, the silica rendered insoluble by prolonged heating of the residue to  $150^{\circ}$ , warmed with hydrochloric acid and water, the silica filtered off, washed with a large quantity of hot water, ignited, and, after weighing, treated with hydrofluoric acid and one drop of sulphuric acid, evaporated, the sulphuric acid evaporated off, the residue ignited, weighed, and the weight of pure silica estimated from the difference.  $\text{SiO}_2 \times 0.4693 = \text{Si}$ .

(c) *Zinc Dust*.—Zinc dust consists of an intimate mixture of finely divided metallic zinc (up to over 90 per cent.) and zinc oxide, together with some cadmium, iron, lead, arsenic, small particles of ground ore, and carbon. In commerce a product containing a guaranteed content of 90 per cent. of metal is usually demanded. The real content of metallic zinc can only be arrived at by a complete analysis. For the technical analysis the reducing action of the zinc on chromic acid, ferric salts, etc., is determined, or the volume of the hydrogen evolved on treatment with dilute acids is measured. Of the many methods proposed, that of Drewson<sup>1</sup> is frequently employed; it depends on the reduction of chromic acid to chromium oxide by the action of dilute

<sup>1</sup> *Z. anal. Chem.*, 1880, 19, 50.

sulphuric acid on zinc dust in presence of a measured quantity of a solution of potassium bichromate of known strength, and titrating back the excess of bichromate with a solution of ferrous sulphate. The equations representing the decompositions are :—



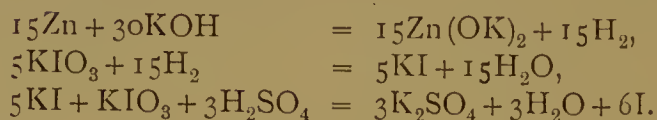
The potassium bichromate solution is prepared by dissolving 40 g. of the pure fused salt in 1 litre, and the ferrous sulphate solution by dissolving about 200 g. of the non-effloresced salt in 1 litre of dilute sulphuric acid (1 : 10). For determining the relation of the two solutions to one another, 20 c.c. of the iron solution are accurately measured out into a beaker, several c.c. of sulphuric acid and 50 c.c. of water added, and the bichromate solution run in from a burette until a drop of the iron solution when brought on to a drop of potassium ferricyanide on a porcelain plate shows no blue or green coloration. It is well to make a preliminary test with 20 c.c. of the iron solution by running in 1 c.c. of the bichromate solution at a time, stirring, taking a drop out, testing, etc., thereby arriving at the approximate amount of bichromate solution required; or this may be calculated from the equation if pure ferrous sulphate or ferrous ammonium sulphate is used.

For the estimation, 0.5 g. of zinc dust are introduced into a beaker, 50 c.c. of the bichromate solution and 5 c.c. of dilute sulphuric acid (1 : 3) added, the mixture stirred round several times, a further 5 c.c. of dilute sulphuric acid added, and frequently stirred for a quarter of an hour. When all but a slight earthy residue is dissolved, 100 c.c. of water, 10 c.c. of distilled sulphuric acid, and 25 c.c. of the ferrous sulphate solution are added, stirred round, and the ferrous sulphate solution run in from the burette, 1 c.c. at a time, stirring between each addition, until a drop of the solution gives a distinct blue coloration with the potassium ferrocyanide. The solution is then titrated back with the bichromate solution until the blue colour disappears. From the total amount of bichromate solution used, the number of cubic centimetres corresponding to the added ferrous sulphate is deducted; the weight of potassium bichromate in the remaining amount of bichromate solution, multiplied by 0.6661, gives the content of metallic zinc. Since the small quantities of metallic iron and cadmium present also reduce corresponding quantities of chromic acid, the content of zinc naturally always comes out too high. Arsenic is determined in zinc dust as in commercial zinc ((b), p. 297).

G. Klemp<sup>1</sup> recommends an iodometric valuation of zinc dust. A small quantity of the zinc dust is dissolved by shaking up with an alkaline solution of potassium iodate, whereby a quantity of iodate

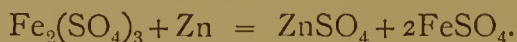
<sup>1</sup> *Z. anal. Chem.*, 1890, 29, 253; *J. Chem. Soc. Abstr.*, 1890, 58, 1190.

corresponding to the metallic zinc is reduced to iodide according to the equations :—



Therefore 6 I corresponds to 15 Zn, or 1 g. I to 1.2876 g. Zn. After the zinc dust has dissolved, the solution is acidified with sulphuric acid, the air driven out by carbon dioxide, the iodine set free distilled off, collected in an aqueous solution of potassium iodide, and titrated with sodium thiosulphate.

A rapid method of valuation, due to Wahl, also depends on the reducing properties of zinc dust. One-half gram is shaken up with water till completely wetted, 15 g. of pure iron alum added, and again shaken up; the contained ferric sulphate is reduced according to the equation :—



After the decomposition, 25 c.c. of sulphuric acid are added, the solution diluted, cooled, made up to 250 c.c., and the ferrous salt in 50 c.c. titrated with permanganate, after the addition of potassium fluoride. It is advisable to pass carbon dioxide through the flask during the decomposition.

R. Fresenius has proposed to determine the content of zinc from the volume of hydrogen evolved on treatment with acids, a method subsequently improved upon by Beilstein and Jawein. F. Meyer<sup>1</sup> has described a special apparatus for this determination. An azotometer (Vol. I., p. 125), nitrometer (Vol. I., p. 132), or gas volumeter (Vol. I., p. 138) may also be employed. A simpler apparatus has been devised by O. Bach.<sup>2</sup> In all these cases the volume of liberated hydrogen must be reduced to normal temperature and pressure and corrected for moisture. Taking the weight of 1 litre of hydrogen as 0.08998 g. and 65.37 as the atomic weight of zinc, the number of cubic centimetres of hydrogen evolved must be multiplied by 0.002918 in order to arrive at the weight of zinc contained in the zinc dust. It is to be borne in mind that in these methods the metallic impurities in the zinc dust (iron and cadmium) react like zinc itself.

### 3. For Alloys.

Alloys containing zinc (brass, tombac, etc.) are analysed by the methods given on pp. 216 *et seq.* Zinc alloyed with a little tin (up to 5 per cent.) is frequently used for castings. For the analysis, 1 to 2 g.

<sup>1</sup> *Z. angew. Chem.*, 1894, 7, 231, 435; *J. Chem. Soc. Abstr.*, 1894, 66, 332, 479.

<sup>2</sup> *Z. angew. Chem.*, 1894, 7, 291; *J. Chem. Soc. Abstr.*, 1894, 66, 400.



are treated with strong nitric acid (which causes the tin oxide to separate in a more dense form than by using the usual acid of sp. gr. 1.2), 100 c.c. of boiling water added, boiled for five minutes, the stannic acid filtered off, and further treated as in the analysis of bronze.

Alloys of zinc and aluminium<sup>1</sup> are analysed as follows:—One-half gram of the drillings is dissolved in a beaker in 25 c.c. of a 25 per cent. sodium hydroxide solution, the contents of the beaker warmed until rapid evolution of gas takes place, and then allowed to stand until solution is complete. The solution is diluted to 300 c.c. with boiling water, and any undissolved iron, copper, lead, tin, or nickel allowed to settle. The clear liquid, which contains nearly all the zinc and aluminium, is decanted, and the residue washed twice by decantation. This residue is dissolved in hydrochloric acid, diluted to 20 c.c., neutralised with sodium hydroxide (1 : 10), and 2 c.c. of the latter added in excess. After warming, the precipitated hydroxides are filtered off and the filtrate and washings added to the main bulk of solution. The zinc is then precipitated by means of sulphuretted hydrogen, the treatment being continued until alumina begins to be precipitated with the zinc sulphide; this point is easily recognised by the formation of a skin at the point where the bubbles of gas burst. The presence of a small amount of alumina (up to 10 per cent.) does not interfere with the ferrocyanide method of determination.<sup>2</sup> The zinc precipitate is allowed to settle, filtered, washed once only, and dissolved in 8 c.c. of hydrochloric acid (1 : 10), the solution diluted to 250 c.c. with boiling water, 5 g. of ammonium chloride added, and the zinc determined by the ferrocyanide method.

Hard zinc, or zinc bottoms from the galvanising of iron, contain up to 6 per cent. of iron and several per cent. of lead. For their analysis several grams of turnings are warmed in a flask with a large excess of dilute sulphuric acid (1 : 5) until the evolution of hydrogen ceases, the solution decanted off from the separated spongy lead, cooled, and the contained iron titrated with permanganate. The lead is dissolved in a little nitric acid, the solution evaporated with sulphuric acid, and the lead determined in the usual way as lead sulphate.

#### 4. For Waste Zinc and Ashes.

A large sample of waste zinc from the melting up of old zinc (fusion ashes), and of zinc ashes from the galvanising of iron (sal-ammoniac slags) is sieved into fine and coarse material, and the latter pounded in an iron mortar until the small pieces of metal are freed from the

<sup>1</sup> R. Seligman and F. J. Willott, *J. Soc. Chem. Ind.*, 1905, **14**, 1278.

<sup>2</sup> Miller and Hall, *Columbia School of Mines Quarterly*, 1900, **21** (iii.), 267.

covering of oxide. The ground-up material is sieved, the coarse and the fine, together with the previously sieved material, weighed separately, and proportionate weighings of each taken so as to give a working sample of 10 g. The sample is dissolved in strong hydrochloric acid (in the case of ashes rich in lead it is better to use nitric acid), and the solution, without filtering, made up to 1 litre. In 100 c.c. of this solution lead and copper are precipitated with sulphuretted hydrogen; the filtrate is boiled to expel the sulphuretted hydrogen, after cooling poured into a large beaker, several drops of Congo red solution added, and neutralised with ammonia until the solution turns a faint red. The solution is then diluted to 600 c.c. and sulphuretted hydrogen passed in to saturation (one and a half to two hours). After standing for several hours, the zinc sulphide is filtered off, further treated as given under Method 1 (p. 288), and finally weighed as sulphide.

*Determination of Chlorine in Sal-Ammoniac Slags.*—An average sample of 5 g. is shaken up for some time in the cold with a large excess of dilute nitric acid (one volume of acid of sp. gr. 1.2 diluted with one volume of water), the solution filtered into a 500 c.c. flask, the flask filled up to the mark, 100 c.c. of the solution taken, and precipitated with an excess of silver nitrate. The silver chloride is finally weighed as such and the content of chlorine calculated.  $\text{AgCl} \times 0.2474 = \text{Cl}$ .

*Zinc-White Residues* consist of coarse particles of zinc oxide together with a little metal and sand. One gram is dissolved in hot hydrochloric acid and a few drops of nitric acid, the solution saturated with ammonia, heated, filtered, and one-fifth of the filtrate titrated with sodium sulphide, or after acidifying with hydrochloric acid, with potassium ferrocyanide solution.

*Residues and Flue dust* are analysed in the same way as ores; flue dust generally contains considerable quantities of lead oxide, lead sulphate, etc., in addition to zinc oxide.

## CADMIUM

*Greenockite*,  $\text{CdS}$ , is the most important of the few cadmium minerals known; it contains 77.6 per cent. of cadmium, is most frequently met with as a yellow earthy deposit on zinc blende, and is of no technical importance; cadmium is found much more frequently as sulphide or carbonate in zinc ores which contain from traces up to 6 per cent. The metal is prepared at zinc smelting works as a by-product in the production of zinc, from zinc fume, from the zinc dust collected in the early stages of the distillation, and from flue dust, and is purified by distillation.

## A. METHODS OF ESTIMATION

## 1. Gravimetric Estimation of Cadmium.

When precipitated from moderately acid solutions with sulphuretted hydrogen, cadmium sulphide, if free from sulphur, may be collected on a weighed filter paper, and after drying at  $100^{\circ}$ , weighed as such. According to T. Fischer,<sup>1</sup> it is precipitated quantitatively, free from zinc, from solutions which contain 10 c.c. of ordinary 25 per cent. hydrochloric acid (sp. gr. 1.125) and 1 g. of crystallised cadmium sulphate per 100 c.c. Cadmium is best determined as sulphate by dissolving the cadmium sulphide in hot dilute nitric acid, evaporating the solution in a weighed crucible with a slight excess of sulphuric acid, driving off the sulphuric acid, and igniting the residue moderately strongly.  $\text{CdSO}_4 \times 0.5392 = \text{Cd}$ .

*Separation of Cadmium from other Metals* (cf. also the Analysis of Commercial Lead, p. 229; Wood's Metal, p. 253; and Spelter, p. 296).—Any lead present is separated as sulphate; if the solution, containing ten to thirteen volumes per cent. of hydrochloric acid (see above), is precipitated with sulphuretted hydrogen and the washed precipitate treated with ammonium sulphide, only copper and bismuth are left to be separated from the cadmium. The sulphides are dissolved in hot, dilute nitric acid, the solution evaporated, the bismuth separated as oxychloride, cadmium and copper precipitated in the filtrate from the bismuth oxychloride with sulphuretted hydrogen, and small quantities of copper dissolved out of the precipitate by means of warm potassium cyanide solution. If much copper is present, the precipitate is dissolved in nitric acid, the solution evaporated, and the copper deposited electrolytically from the solution containing over 5 per cent. of sulphuric acid; or, the nitric acid solution is neutralised with potassium or sodium hydroxide, warmed with an excess of potassium cyanide, the cadmium precipitated as sulphide by the addition of a little ammonium sulphide solution, and finally estimated as cadmium sulphate. Cadmium is separated from large quantities of zinc, and smaller quantities of iron and manganese (solutions of ores) by warming the solution, after the separation of the lead as sulphate, with a good excess of sodium hydroxide, diluting, cooling, filtering, washing the precipitate with water containing some sodium hydroxide, extracting the cadmium hydroxide, with ammonia, neutralising the ammoniacal solution, adding ten volumes per cent. of hydrochloric acid, passing in sulphuretted hydrogen, in the cold, and thus precipitating pure cadmium sulphide, which is converted into sulphate. In solutions of common calamine containing much iron and aluminium, the lead is separated, the filtrate treated with

<sup>1</sup> Private communication to Prof. Pufahl.



sulphuretted hydrogen, the zinc sulphide containing cadmium sulphide dissolved in a measured quantity of hot hydrochloric acid, the solution diluted until it contains 10 volumes per cent. of hydrochloric acid, and then pure cadmium sulphide precipitated by means of sulphuretted hydrogen.

## 2. Electrolytic Estimation of Cadmium.

Cadmium may be determined electrolytically from its solution in various electrolytes. A potassium cyanide solution is very largely used for this purpose. The cadmium from 1 g. of ore is first obtained as chloride or sulphate solution free from other metals, precipitated in acid solution by sulphuretted hydrogen, and the solution evaporated, if necessary, to 100 c.c. or less. A few drops of phenolphthalein solution are added, and then pure sodium or potassium hydroxide solution, until a permanent red colour is obtained. A concentrated solution of pure potassium cyanide is then added until the precipitated cadmium hydroxide is completely dissolved; an excess must be avoided. The solution is diluted to 100 to 125 c.c., heated to 60°, and electrolysed with a current of  $CD_{100} = 0.04$  to  $0.06$  ampère at 2.9 to 3.2 volts. The deposition is usually complete in from four to six hours; when finished, the electrode is washed with hot water, then with alcohol, and finally dried at 100° and weighed. The deposition can also be effected from a sulphate solution.<sup>1</sup>

## B. ANALYSIS OF ZINC ORES AND OF METALLURGICAL PRODUCTS CONTAINING CADMIUM

*Ores, Zinc fume, and Flue dust.*—W. Minor<sup>2</sup> dissolves ores, etc., in hydrochloric acid or aqua regia; the solution is evaporated with excess of sulphuric acid to separate the lead, filtered, and sulphuretted hydrogen passed into the filtrate, whereby cadmium sulphide containing zinc sulphide is precipitated. The precipitate is dissolved in hot hydrochloric acid, the sulphuretted hydrogen driven off, hot sodium hydroxide solution added, the solution boiled, the cadmium hydroxide filtered off, washed first with 1 per cent. sodium hydroxide solution, then with hot water, dried, the filter paper ashed in a Rose's crucible at a moderate heat, the lid placed on, and oxygen led into the crucible, which is ignited to a dull red heat. The cadmium oxide remaining is weighed.  $CdO \times 0.8754 = Cd$ . If the filter ash be heated too strongly, some cadmium may volatilise; it is better, therefore, to dissolve the washed hydroxide in hot, dilute hydrochloric acid, evaporate the solution

<sup>1</sup> Cf. E. F. Smith, *Electro-Analysis*, p. 82; and Kallcock and Smith, *J. Amer. Chem. Soc.*, 1899, 21, 925.

<sup>2</sup> *Chem. Zeit.*, 1890, 14, 4, 34, 348; *J. Chem. Soc. Abstr.*, 1891, 60, 112.

down in a weighed porcelain crucible with a slight excess of sulphuric acid, and estimate the cadmium as sulphate (p. 303).

If sodium thiosulphate is added to a hot hydrochloric or sulphuric acid solution of a zinc ore and the solution boiled, no cadmium sulphide is precipitated.

*Zinc dust.*—An average sample of from 20 to 40 g. is dissolved in a moderate excess of hydrochloric acid, the solution filtered, 50 or 100 c.c. of the filtrate (made up to 1 or 2 litres) taken, diluted to 300 to 500 c.c., sulphuretted hydrogen passed in, the precipitated cadmium sulphide, containing zinc, dissolved in a measured quantity of hot hydrochloric acid, the solution diluted so as to contain ten volumes per cent. of hydrochloric acid, pure cadmium sulphide precipitated with sulphuretted hydrogen, and weighed as sulphate as above.

*Crude Zinc and Spelter.*—A large sample (50 to 100 g.) is warmed with insufficient dilute sulphuric acid to effect complete solution, the solution decanted off, the residue containing all the cadmium and lead dissolved in dilute nitric acid, the solution evaporated with a slight excess of sulphuric acid, the residue taken up with water, and the lead sulphate filtered off; ten volumes per cent. of hydrochloric acid (sp. gr. 1.125) are added to the filtrate, sulphuretted hydrogen passed in for one hour, the precipitate filtered off, and hot hydrochloric acid poured over the filter paper (whereby any copper sulphide present remains undissolved). The solution is diluted proportionately and pure cadmium sulphide precipitated by means of sulphuretted hydrogen, etc., or the hydrochloric acid solution is directly evaporated with sulphuric acid and the cadmium sulphate weighed.

### C. METALLIC CADMIUM

The commercial metal generally contains about 99 per cent. of cadmium; the chief impurities are zinc, a little lead and iron, and less frequently copper.

For the analysis, 2 g. are dissolved in a covered dish by warming with 50 c.c. of 10 per cent. sulphuric acid with the addition of some nitric acid, the solution evaporated, the residue taken up with water, the lead sulphate filtered off, and the copper deposited electrolytically from the filtrate in a large platinum crucible. The solution, freed from copper, is diluted in a beaker to about 400 c.c., 40 c.c. of hydrochloric acid (sp. gr. 1.125) added, sulphuretted hydrogen passed in for a long time, until all the cadmium is precipitated as sulphide, which is filtered off and washed with dilute sulphuretted hydrogen water containing ten volumes per cent. of hydrochloric acid. The filtrate from the cadmium sulphide is evaporated to drive off the hydrochloric acid and most of the sulphuric acid, the cooled residue taken up with water, and

a slight excess of sodium carbonate added. The solution is boiled for ten minutes, the zinc carbonate containing iron filtered off and washed with hot water; the filter paper is dried and the contents of the paper removed as completely as possible. The paper is then ignited in a weighed porcelain crucible, the zinc carbonate transferred to the crucible, ignited, and weighed. After weighing, the impure zinc oxide is dissolved in hydrochloric acid, the solution diluted, warmed to  $70^{\circ}$ , potassium iodide added, cooled, and the free iodine titrated in presence of starch with a standard solution of sodium thiosulphate. The iron so determined is deducted, as  $\text{Fe}_2\text{O}_3$ , from the weight of impure zinc oxide.

#### D. CADMIUM ALLOYS

The fusible alloys containing cadmium are analysed in the same way as Wood's metal (*cf.* Bismuth, p. 253). For some years past, much cadmium has been used in the preparation of a solder for aluminium. Traces of cadmium as well as of bismuth and tin may, therefore, frequently be found in "old aluminium." In the analysis of the cadmium amalgams used in dentistry, the mercury cannot be determined by distillation on account of the volatility of cadmium. One gram of the amalgam is dissolved in nitric acid, the solution evaporated, the residue taken up with dilute hydrochloric acid, the mercury precipitated as mercurous chloride with phosphorous acid (phosphorus, trichloride and water), and after diluting the filtrate with water, the cadmium is precipitated as sulphide by passing in sulphuretted hydrogen, etc.

#### NICKEL AND COBALT

These metals, which are so very similar in their chemical behaviour, are always found associated together, both in their ores and in the metallurgical products produced therefrom. By carrying out either a dry or wet assay, a mixture of the two, together with other elements, is also always obtained. Ores poor in copper yield very good results when carefully assayed by Plattner's dry methods,<sup>1</sup> which are employed for the working assays in nickel and cobalt works. For the accurate determination of nickel, cobalt, and the other associated metals, and of the impurities, gravimetric methods are generally employed, and the two metals themselves are separated together electrolytically.

**Ores.**—The most important ores are:—

*Kupfernickel*,  $\text{NiAs}$ , containing 43.5 per cent. of nickel; the arsenic is largely replaced (up to 28 per cent.) in many varieties by antimony.

<sup>1</sup> *Cf.* Kerl, *Metallurgische Probierkunst*, 2nd ed., and *Probierbuch*, 3rd ed.; also Ricketts and Miller, *Notes on Assaying*, 3rd ed., 1902, p. 84.



*Chlorcenthite*,  $\text{NiAs}_2$ , containing 28.2 per cent. of nickel; nickel is frequently replaced by cobalt and iron (up to 17 per cent. iron).

*Nickel Blende*, *Millerite*,  $\text{NiS}$ , containing 64.5 per cent. of nickel.

*Antimonial Nickel*,  $\text{NiSb}$ , containing 32.2 per cent. of nickel.

*Antimonial Nickel Ore*, *Ullmanite*,  $\text{NiSbS}$ , containing 27.35 per cent. of nickel. *Arsenical Nickel Ore*,  $\text{NiAsS}$ , containing 35.15 per cent. of nickel.

*Nickel Magnesium Silicates*, containing water. *Rewdanskite*, containing up to 18 per cent. of nickel. *Garnierite*, with up to 30 per cent. of nickel; and many similar silicates containing nickel. *Magnetic pyrites*, *Iron pyrites*, and *Copper pyrites*, containing nickel, are found in large quantities.

*Speiss Cobalt*,  $\text{CoAs}_2$ , when pure containing 28 per cent. of cobalt, very frequently containing considerable quantities of iron and nickel.

*Cobalt Glance*,  $\text{CoAsS}$ , containing 35.5 per cent. of cobalt, frequently with a high content of iron.

*Cobalt Nickel Blende*,  $2\text{RS}$ ,  $3\text{R}_2\text{S}_3$  ( $\text{R} = \text{Ni}, \text{Co}, \text{Fe}$ ), containing 11 to 40.7 per cent. of cobalt and 14.6 to 42.6 per cent. of nickel.

*Earthy Cobalt* or *Wad*  $(\text{CoMn})\text{O}$ ,  $2\text{MnO}_2 \cdot 4\text{H}_2\text{O}$ , containing up to 15 per cent. of cobalt.

#### A. SEPARATION OF NICKEL AND COBALT FROM OTHER METALS AND COMBINED SEPARATION OF BOTH AS METALS

Finely ground ores, speisses, and mattes are dissolved in a flask by warming with aqua regia (20 c.c. for 1 g. of substance), the solution boiled, the residue evaporated to dryness with hydrochloric acid, taken up again with dilute hydrochloric acid, and arsenic, antimony, copper, lead, bismuth, etc., precipitated by passing sulphuretted hydrogen for some time into the gently warmed solution. The solution of arsenical ores and speisses is previously repeatedly boiled with additions of sulphurous acid so as to reduce all arsenic oxide to arsenious oxide, and then treated with sulphuretted hydrogen; a previous roasting of such substances is also to be recommended, whereby the greater part of any arsenic, antimony, and sulphur present is removed. The powdered substance, spread out on a scorifying dish, is first roasted in a muffle to a dull red heat, the cooled, roasted material then mixed with an equal volume of powdered wood charcoal, the roasting again carried out at a higher temperature, and again repeated.

Pyrites and mattes poor in nickel and cobalt are also first roasted "sweet," if it is desired to treat their solution by Rothe's method, p. 9.

For the determination of any zinc present, the sulphuretted hydrogen in the filtrate from the sulphide precipitates is boiled off,

bromine water added, the cooled solution nearly neutralised in the presence of a few drops of Congo red solution, and the zinc precipitated as sulphide by passing in sulphuretted hydrogen for a long time (*cf.* p. 288). The filtrate from the zinc sulphide is evaporated over a free flame, the iron oxidised in the concentrated solution with a little nitric acid, the cooled solution neutralised with sodium hydroxide or sodium carbonate solution, sodium acetate (six times the weight of the suspected iron content) added, the solution largely diluted with water, heated to boiling, and boiled for five minutes. The bulky precipitate containing all the iron and aluminium as basic acetates is filtered off and washed with hot water. Since the precipitate always retains some nickel and cobalt, it must be dissolved at least once and reprecipitated by boiling with sodium acetate after neutralisation; if the substance contains much iron, nickel may be detected in the filtrate after reprecipitating four times. The combined filtrates are heated in a porcelain dish, and sodium hydroxide and bromine water added in excess. After the dark brown precipitate containing all the nickel, cobalt, and manganese has separated out, it is filtered off, washed with hot water, dissolved in hot, dilute sulphuric acid to which some sulphurous acid is added, and the solution evaporated on the water-bath. If the manganese present does not amount to more than a few per cent., the solution is washed into a beaker of 200 c.c. capacity, a large excess of ammonia (30 to 50 c.c.) added, together with 30 c.c. of a cold, saturated solution of ammonium sulphate,<sup>1</sup> the solution of about 150 c.c. stirred, a platinum cone and spiral placed in the beaker, and the nickel and cobalt deposited electrolytically by means of a current of 2.8 to 3.3 volts and 0.5 to 1.5 ampères per 100 sq. cm. of cathode surface, at the ordinary temperature. All the manganese separates as hydrated manganese dioxide, which floats about as a flocculent precipitate in the liquid and only adheres to the spiral to a very slight extent.

A higher percentage of manganese interferes with the electrolysis. In this case the solution containing the sulphates of nickel, cobalt, and manganese (see above) is washed into a pressure-bottle of about 500 c.c. capacity, neutralised with ammonia, 30 c.c. of a solution of ammonium acetate, prepared by neutralising acetic acid with ammonia, and 20 c.c. of 50 per cent. acetic acid added, diluted to 300 to 400 c.c., sulphuretted hydrogen passed in for from one to two hours, the stopper screwed down, the bottle placed in a cold water-bath, and this latter heated to boiling within half an hour. Nickel and cobalt separate as black sulphides, which adhere to some extent to the sides of the bottle. The bottle is allowed to cool to about 50° in the water-bath, then taken out, the stopper removed, the sulphides filtered off, washed with water

<sup>1</sup> Fresenius and Bergmann's method, *Z. anal. Chem.*, 1879, 19, 314; Fresenius, *Quantitative Analysis*, 7th ed., vol. ii., p. 304.

to which some acetic acid and sulphuretted hydrogen water is added, the sulphides washed off the filter paper into a porcelain dish, and the water evaporated off. The filter paper is ignited and the ash added to the contents of the dish, in which (after covering with a clock-glass) the sulphides of nickel and cobalt are dissolved by warming with strong nitric acid with the addition of a little hydrochloric acid. The sulphides remaining in the bottle are likewise dissolved in hot aqua regia, the solution washed into the dish, an excess of 50 per cent. sulphuric acid added, the solution evaporated, the residue taken up with water, the pale yellow separated sulphur filtered off, the filtrate saturated with excess of ammonia, a large quantity of ammonium sulphate (see above) added, and the nickel and cobalt then deposited electrolytically, using a cylinder, cone, dish, or crucible (*cf.* The Electrolytic Determination of Copper, p. 159). When from several decigrams up to 2 g. of nickel and cobalt are to be deposited, the solution is tested for complete deposition after six to twelve hours, according to the strength of current employed, by withdrawing 1 to 2 c.c. by means of a pipette, adding a few cubic centimetres of sulphuretted hydrogen water, and warming in a test tube; if no yellow or brown coloration is produced the deposition is complete. It is to be specially noticed that the complete deposition by means of the current is considerably hindered by the presence of small quantities of nitrates or chlorides in the solution. The washing is carried out without breaking the current. The cathode is repeatedly washed with distilled water, finally with absolute alcohol, the dish or crucible dried on a boiling water-bath, the cylinder or cone over a heated dish, and the cathode weighed after cooling for half an hour. Pufahl considers the much-advocated use of ether for drying electrolytic metallic deposits as quite superfluous, especially as ether is an oxygen carrier. Electrolytically deposited nickel is purely metallic, and possesses a yellowish gray colour; cobalt is of a darker gray colour, and, according to C. Winkler,<sup>1</sup> always contains some oxygen, up to 1.88 per cent. of the total amount of cobalt being deposited as hydrated cobaltic oxide. This does not appreciably influence the accuracy of the technical determination.

When nickel and cobalt are deposited quickly by electrolysis, using a current of from 1 to 1.5 ampères, the solution becomes very hot and much ammonia is lost; in order to prevent this, the crucible used as cathode, for example, is cooled by immersion in a platinum dish partially filled with water.

The rapid electrolytic deposition of cobalt and nickel, using a rotating anode, is described by E. F. Smith.<sup>2</sup> Previous to the introduction of the electrolytic separation, nickel and cobalt were usually precipitated from

<sup>1</sup> *Z. anorg. Chem.*, 1894, 8, 1, 291; *J. Chem. Soc. Abstr.*, 1895, 68, 167.

<sup>2</sup> *Electro-Analysis*, pp. 126-133.



the solution of the sulphides by excess of pure sodium hydroxide, heating, and then adding chlorine or bromine water. - The precipitates of the hydrates of the sesquioxides were collected on an ash-free filter paper, persistently washed with hot water, dried, the filter paper ignited in a small platinum crucible exclusively used for the purpose, and then the oxides added and reduced by prolonged, strong ignition in a current of hydrogen. Since it is impossible to prevent some alkali being retained by the precipitate, the spongy metal must be extracted with hot water and then dried in an air-bath.

The accurate determination of nickel and cobalt in substances rich in iron is especially tedious, since, even in very dilute solutions, the precipitate of basic ferric acetate (or sulphate) carries down with it considerable quantities of nickel and cobalt, and does not separate in a pure condition (*e.g.*, in the analysis of nickel steel) until after the fourth or fifth precipitation. This great inconvenience is completely overcome by the use of J. Rothe's ether method (p. 9). The method requires the presence of all iron as ferric chloride in concentrated hydrochloric acid solution. The filtrate from the sulphuretted hydrogen precipitates is evaporated, oxidised with nitric acid, evaporated on the water-bath, the evaporation repeated with 30 to 50 c.c. of hydrochloric acid, the syrupy liquid brought into the Rothe's extraction apparatus, and the dish washed out three times with small quantities of pure hydrochloric acid of sp. gr. 1.1 (20 per cent.). If the substance contains a high percentage of iron (*e.g.*, pyrites or magnetic pyrites poor in nickel), for every gram of iron assumed to be present, 6 c.c. of fuming hydrochloric acid saturated (by shaking whilst cooling) with ether are added; in the case of a moderate percentage of iron, this addition is not necessary. Seventy-five to one hundred c.c. of alcohol-free ether are then run in, the apparatus cooled under the tap, violently shaken, and then allowed to remain still for five minutes. All the iron (excepting 1 to 2 mg.) goes into the ether, and nickel, manganese, aluminium, and practically all the cobalt into the aqueous hydrochloric acid solution. After running off the aqueous hydrochloric acid solution, the ethereal ferric chloride solution in the top bulb is repeatedly shaken up with 10 c.c. of hydrochloric acid of sp. gr. 1.1, saturated with ether, and by this means all the cobalt is extracted in a short time. In order to remove the small amount of ferric chloride retained by the aqueous hydrochloric acid solution in the lower bulb, the solution is shaken up with 75 to 100 c.c. of ether. It is then run out into a shallow porcelain dish (15 cm. in diameter), an excess of 50 per cent. sulphuric acid added, gently warmed on the water-bath (quarter of an hour) to drive off the dissolved ether, evaporated, the evaporation repeated with the addition of several cubic centimetres of water, the residue taken up with water, excess of ammonia and ammonium sulphate added, and the solution electrolysed as above.

If the substance contains much manganese, aluminium, and magnesium, as well as some zinc, it is well to precipitate the aluminium by boiling with sodium acetate; in the filtrate, to which some ammonium acetate and acetic acid are added, nickel and cobalt are precipitated as sulphides in a pressure bottle as described above. Any zinc sulphide precipitated with the nickel and cobalt is dissolved by treating the sulphides with hot, dilute hydrochloric acid, to which some sulphuretted hydrogen water is added; the pure sulphides of nickel and cobalt are then dissolved in aqua regia, the solution evaporated with excess of sulphuric acid, and finally electrolysed.

According to an old method, due to Mackintosh,<sup>1</sup> which is sufficiently accurate for technical purposes, the nickel and cobalt in substances either poor or rich in iron are determined by adding a slight excess of ammonia to the hydrochloric acid filtrate from the sulphuretted hydrogen precipitate, then adding a considerable quantity of ammonium sulphide, warming, and then digesting for some time with a large excess of 5 per cent. hydrochloric acid; the sulphides of iron, zinc, manganese, and traces of nickel and cobalt sulphides are dissolved, together with alumina. The residue (sulphides of nickel and cobalt with a little iron sulphide), after being washed with sulphuretted hydrogen water, slightly acidified with hydrochloric acid, is dissolved in aqua regia, the solution evaporated with sulphuric acid until fumes are evolved, the residue taken up with water, ammonia added, and nickel and cobalt deposited electrolytically.

In ores containing a high percentage of manganese, W. Witter<sup>2</sup> determines the nickel and cobalt as follows:—Iron and aluminium are precipitated as usual as basic acetates in the combined filtrates, and nickel, cobalt, and manganese by warming with sodium hydroxide and bromine water; the latter precipitate is then dissolved, and the solution electrolysed. When most of the nickel and cobalt (after several hours) is deposited, the cone is washed, dried, and weighed. The solution is warmed in a beaker with the addition of hydrochloric acid until all the hydrated manganese dioxide has dissolved, ammonia and ammonium sulphide added, again warmed, acidified with 5 per cent. hydrochloric acid (which dissolves all the manganese sulphide), and filtered, etc., as above. By this means all the nickel and cobalt retained by the manganese dioxide is separated, which is not the case even by very prolonged electrolysis.

<sup>1</sup> *Chem. News*, 1887, 56, 64.

<sup>2</sup> Private communication to Prof. Pufahl.

B. SEPARATION OF NICKEL FROM COBALT<sup>1</sup>

## 1. QUANTITATIVE SEPARATION AND DETERMINATION OF COBALT

## (a) By Potassium Nitrite (Fischer and Stromeyer).

The electrolytic deposit of the two metals is dissolved off the electrode in hot, dilute nitric acid (one volume of acid of sp. gr. 1.2 to three volumes of water), and the solution evaporated in a porcelain dish on the water-bath. The residue is taken up in a few cubic centimetres of water, 5 g. of potassium nitrite added (in cold, saturated aqueous solution), and then acetic acid until nitrous acid is evolved. The cobalt separates as brownish yellow potassium cobaltinitrite; the precipitation is complete after standing about twenty-four hours. The cobalt compound is then filtered off, washed with a cold, saturated solution of potassium sulphate, dissolved in hot, dilute sulphuric acid, the rose-red solution evaporated on the water-bath, washed into a large platinum crucible, a large excess of ammonia added together with a considerable quantity of ammonium sulphate, the cobalt deposited electrolytically, and the nickel estimated by difference. If nickel and cobalt have been determined by the reduction of the sesquioxides in a platinum crucible, the spongy metals are shaken out, dissolved, etc., and the crucible again weighed; by strong ignition in hydrogen, some nickel and cobalt alloy superficially with the platinum. This method is suited to all cases, especially when much cobalt is present together with a little nickel.

The filtrate from the potassium cobaltinitrite may be heated with excess of hydrochloric acid, diluted, saturated with sodium hydroxide, bromine water added, and the solution warmed so as to precipitate the nickel as the hydroxide, which is washed, dried, and reduced in hydrogen; or, the precipitate is dissolved in dilute sulphuric acid and aqueous sulphurous acid, evaporated, and the pure nickel deposited electrolytically.

(b) By Nitroso- $\beta$ -Naphthol (M. Ilinski and G. von Knorre<sup>2</sup>).

Nitroso- $\beta$ -naphthol forms compounds with nickel and cobalt, the cobalt compound, cobalti-nitroso- $\beta$ -naphthol  $[\text{C}_{10}\text{H}_6\text{O}(\text{NO})]_3\text{Co}$ , being insoluble in dilute hydrochloric acid. The solution of the two metals in dilute nitric acid is evaporated down with a slight excess of sulphuric

<sup>1</sup> Cf. C. Krauss, *Z. anal. Chem.*, 1891, 30, 227; *J. Chem. Soc. Abstr.*, 1891, 60, 1139. This paper contains a summary and critical examination of methods for the separation and estimation of cobalt and nickel.

<sup>2</sup> *Ber.*, 1885, 18, 699; *J. Soc. Chem. Ind.*, 1885, 4, 370; Cf. also *Chem. Zeit.*, 1895, 19, 1421; *J. Soc. Chem. Ind.*, 1896, 15, 51.



acid, and the nitric acid completely driven off. The residue is dissolved in water, 5 c.c. of ordinary hydrochloric acid added, the solution warmed, and a freshly prepared hot solution of nitroso- $\beta$ -naphthol in 50 per cent. acetic acid added until after the precipitate has subsided, a fresh addition of the solution produces no further precipitate. After digesting for several hours at a gentle heat, the very bulky precipitate of the cobalti-compound and much nitroso- $\beta$ -naphthol is filtered off, washed first with cold, then with warm 12 per cent. hydrochloric acid, and finally with hot water. The filter is then folded together, placed in a weighed platinum crucible, the lid placed on, and the crucible heated with a large Bunsen burner. When no more combustible gases are evolved, the lid is removed, the crucible placed in a slanting position, and the difficultly combustible coke-like carbon completely ignited away; this requires from half an hour to an hour. If care be taken to give good access of air, the cobalt is left behind as tri-cobaltic tetroxide,  $\text{Co}_3\text{O}_4$ , of a black colour; reducing gases from the burner may cause considerable quantities of cobaltous oxide, and even of metallic cobalt to be formed.  $\text{Co}_3\text{O}_4 \times 0.7343 = \text{Co}$ .

The method gives excellent results; on account of the bulkiness of the cobalti-compound, large quantities of cobalt are best precipitated according to the nitrite method.

## 2. QUANTITATIVE SEPARATION AND DETERMINATION OF NICKEL

### (a) By Dimethylglyoxime.

This method is described under "Nickel" in the section on "Iron," this volume, Part I., p. 66.

### (b) By Dicyanodiamidine.

This method is also described under "Nickel" in the section on "Iron," this volume, Part I., p. 67.

## 3. DETECTION OF COBALT

To the hydrochloric acid solution free from nitric acid, an equal volume of alcohol is added, the solution warmed, freshly prepared nitroso- $\beta$ -naphthol solution added, and the solution boiled when the purple-red cobalti-nitroso- $\beta$ -naphthol separates; very small traces are only precipitated after standing for some time. Any brown nitroso- $\beta$ -naphthol which separates may be dissolved by warming with 50 per cent. acetic acid.

## 4. DETECTION OF NICKEL

To the ammoniacal cobalt solution containing nickel, ammonium chloride and some sodium hypochlorite are added and the solution

warmed. The cobalt is rapidly oxidised, and is contained in the dark reddish yellow solution essentially as a luteo-salt. If potassium hydroxide be added to the cooled and diluted solution, a cloudiness due to the separation of nickelous hydroxide is produced if nickel be present.

According to L. Tschugaeff,<sup>1</sup> dimethylglyoxime is the most delicate reagent for the detection of nickel. It is added to the neutral or slightly ammoniacal solution, which is then boiled for a short time; a scarlet precipitate is formed, or, with only traces of nickel, a yellowish solution, from which the red precipitate separates on cooling. Distinct indications are obtained with solutions containing only 1 part of nickel in 400,000 parts of water.

### C. SPECIAL METHODS

#### 1. Ores, etc.

*Ores and Speisses containing Arsenic and Antimony* are dissolved either by warming with nitric acid or with aqua regia, or (according to Hampe) in nitric and tartaric acids; the addition of tartaric acid is especially advisable if it is desired to carry out a complete analysis; Hampe takes 30 c.c. of ordinary nitric acid, and 10 g. of tartaric acid for 1 g. of speiss, etc. For the determination of copper, nickel, and cobalt, it is advisable to first roast the substance, then to dissolve it in aqua regia, boil the solution, heat the residue gently with hydrochloric acid, pass sulphuretted hydrogen in for a long time after diluting, and further treat the filtrate from the sulphuretted hydrogen precipitates as described above (p. 307). If the substance contains a high percentage of iron, the Rothe method (p. 9) is applied.

*Pyrites containing Nickel, Magnetic Pyrites, and Nickel Matte* are likewise best roasted first, and the finely ground product dissolved in aqua regia, etc., as above.

*Garnierite and similar Silicates* are either fused in a platinum crucible with three to four times the weight of potassium sodium carbonate and some nitre, or with six times the weight of potassium hydrogen sulphate. The alkaline melt is lixiviated with water, evaporated to dryness with excess of hydrochloric acid, the silica rendered insoluble, the copper precipitated in the hydrochloric acid filtrate by means of sulphuretted hydrogen, and in the filtrate from the copper sulphide, aluminium, iron, manganese, calcium, and magnesium, separated as described above (p. 310). The fusions obtained with potassium hydrogen sulphate and nitre are treated with water and hydrochloric acid, the silica filtered off, the copper precipitated in the filtrate with sulphuretted hydrogen, etc., as above. Very

<sup>1</sup> *Ber.*, 1905, 38, 2520; *J. Soc. Chem. Ind.*, 1905, 24, 941.

finely ground garnierite may also be decomposed by boiling with hydrochloric acid, aqua regia, or 50 per cent. sulphuric acid. The sulphuric acid or other solution to which sulphuric acid is added is boiled until fumes of sulphuric acid commence to be evolved, the cooled mass then treated with water, filtered, the copper precipitated from the filtrate, etc.

The sulphuric acid filtrate from the copper sulphide precipitate is boiled finally, with the addition of a few drops of bromine water, cooled, transferred to a beaker, a large excess of ammonia added, and, if necessary, also some ammonium sulphate, and nickel and cobalt deposited electrolytically on a cone. The considerable quantities of earths and magnesia, as well as the manganese present, are without influence; if much iron is present, some may be deposited as metal, together with nickel and cobalt. The nitric acid solution of the nickel and cobalt is afterwards tested by saturating with ammonia, filtering off any ferric hydroxide which separates, which is weighed as ferric oxide, and the calculated quantity of iron deducted.  $\text{Fe}_2\text{O}_3 \times 0.6994 = \text{Fe}$ .

*Nickel Copper Matte.*—(a) One to two grams of the matte are dissolved in aqua regia, the solution boiled, the residue warmed with hydrochloric acid, water added, again boiled, and the copper precipitated as sulphide with sodium thiosulphate. The sulphur dioxide is expelled from the filtrate from the copper sulphide by boiling, the ferrous salt oxidised, the cooled solution neutralised with sodium hydroxide, sodium acetate added, etc., as described above. If the matte contains lead, the solution in aqua regia is evaporated with sulphuric acid, the residue taken up with water, the lead sulphate filtered off, the filtrate boiled, sodium thiosulphate added, etc., as above.

(b) One to two grams are roasted, the product dissolved in aqua regia, the solution evaporated down, the evaporation repeated with hydrochloric acid (20 to 40 c.c.), the concentrated solution introduced into Rothe's extraction apparatus (*cf.* p. 310), the solution containing copper, nickel, cobalt, and manganese evaporated with sulphuric acid, and the copper deposited electrolytically; the solution, free from copper, is then evaporated to drive off the nitric acid, the residue dissolved in water, saturated with ammonia, and the nickel and cobalt deposited electrolytically. Any zinc present is precipitated with sulphuretted hydrogen, after neutralising the solution from the copper deposition with ammonia, making just acid with sulphuric acid, and diluting. Small quantities of lead are found with the copper, nickel, and cobalt, and are separated by evaporating with sulphuric acid; if the lead amounts to more than several tenths per cent. it is better to precipitate the copper and lead together from the diluted hydrochloric acid solution by means of sulphuretted hydrogen, and then to separate the sulphides in the usual way (lead as sulphate and copper electrolytically).



as metal), drive off the sulphuretted hydrogen from the filtrate from the sulphides, oxidise, evaporate, and extract the concentrated solution with ether.

*Slags* (e.g., from the refining of copper containing nickel, etc.) are decomposed with aqua regia, the solution evaporated, the filtrate from the silica treated with sulphuretted hydrogen, the sulphides filtered off, the sulphuretted hydrogen boiled off from the filtrate, which is then oxidised, neutralised with sodium hydroxide, and the iron and aluminium precipitated in the usual way. The nickel and cobalt in the filtrate are precipitated as the hydroxides with sodium hydroxide and bromine, the hydroxides dissolved, and the metals deposited electrolytically in presence of manganese.

*Smalts*.—One gram of the fine powder is stirred up in a platinum dish with 5 c.c. of 50 per cent. sulphuric acid, about 20 c.c. of hydrofluoric acid added, gently warmed for one hour on the water-bath, then evaporated, and heated on a sand-bath until sulphuric acid fumes are evolved. The cooled residue is taken up with water, any separated lead sulphate filtered off, and sulphuretted hydrogen passed into the filtrate, whereby copper, arsenic, and bismuth may be precipitated. After boiling off the sulphuretted hydrogen from the filtrate, the iron is oxidised with nitric acid and subsequently precipitated as basic acetate together with the aluminium. Cobalt (nickel and manganese) is precipitated from the filtrate with sodium hydroxide and bromine water, the hydroxides washed, dissolved in dilute sulphuric acid containing some sulphurous acid, and after evaporating, etc., the cobalt and nickel deposited electrolytically. The flocculent precipitate of hydrated manganese dioxide is collected on a filter paper, dried, the paper ignited, and the strongly ignited trimanganic tetroxide weighed. Cobalt and nickel are dissolved from the cathode and separated by means of potassium nitrite according to method **a** (p. 312).

*Sulphur* is determined in ores, mattes, and speisses by Hampe's method (p. 195).

## 2. Commercial Nickel.

The metal comes on to the market as a fritted spongy mass in the form of small cubes and round cylinders about 30 mm. high and 50 mm. diameter, and in a fused condition in the form of anode plates and granulated metal, and also as granules from the Mond process.

The impurities (iron, arsenic, sulphur, silicon, and carbon) amount usually to less than 1 per cent.; cobalt, to the extent of usually about 1 per cent. but frequently in considerably larger quantities, is always present, whilst manganese finds its way into the metal through the refining processes, and is hardly to be considered as an impurity. Fused nickel manufactured by the Fleitmann patents contains traces of

magnesium (about 0.1 per cent.). Tin is seldom met with; W. Witter<sup>1</sup> found considerable quantities of tin in nickel cubes from Japan. Fused nickel may contain several per cent. of carbon and some silicon; in the fritted metal the greater part of the carbon appears to be free. By the reduction of nickel oxide by means of flour, etc., the latter introduces into cube nickel small quantities of lime, alumina, alkalis, and sand.

Nickel-copper containing up to 30 per cent. of copper, which cannot be distinguished by its colour from nickel, is prepared in some works for the manufacture of German silver, and comes on to the market in a granulated form.

*Analysis.*—In the case of nickel cubes and small cylinders of nickel, small pieces are chipped off by means of a sharp chisel; the granulated metal is used as such or the granules are divided by a chisel; in the case of anode plates borings are taken. Tin is tested for by dissolving about 1 g. of the metal in nitric acid in a large test tube, diluting with water, and boiling; if tin is present, 5 g. of the metal are dissolved in a dish in 40 c.c. of nitric acid (sp. gr. 1.4), treated as in the case of a bronze analysis (pp. 208 *et seq.*), the stannic oxide ignited in a platinum crucible, and, after weighing, treated with hydrofluoric acid and one drop of sulphuric acid to remove any admixed silica. The filtrate from the meta-stannic acid is evaporated with excess of sulphuric acid and treated as described below. If the metal dissolves to a nearly clear solution in nitric acid, 10 g. are weighed out, treated in a covered porcelain dish with 70 c.c. of nitric acid (sp. gr. 1.4), and 10 c.c. of water, warmed on the water-bath until completely dissolved, 40 c.c. of 50 per cent. sulphuric acid added, the solution evaporated, and finally heated on a sand-bath until fumes of sulphuric acid commence to be evolved. The cooled residue is dissolved by heating on a boiling water-bath and stirring, and the silica (sand and some charcoal) filtered off. Fused nickel contains silicon. If the metal contains much copper, this is deposited from the sulphate solution electrolytically, after the addition of nitric acid. The filter paper containing the silica is ignited in a weighed platinum crucible, the weighed silica gently warmed for a long time with hydrofluoric acid and one drop of sulphuric acid (sand dissolves but very slowly), the solution evaporated, the sulphuric acid driven off, and the residue, consisting at most of a little ferric oxide, ignited and weighed. Sulphuretted hydrogen is passed into the warmed sulphate solution for a long time and the copper thereby precipitated as sulphide, which is dissolved in nitric acid, the copper deposited electrolytically, and the electrolysis continued longer than necessary for the deposition of the copper, so as to see whether any arsenic is present. If only a few milligrams of copper are precipitated, the copper sulphide is roasted to oxide in a porcelain crucible, and weighed as such.

<sup>1</sup> Private communication to Prof. Pufahl.

If arsenic is found to be present, the sulphate solution, free from nitric acid, prepared from 10 or 20 g. of the metal, is brought into a flask, 5 to 10 g. of ferrous sulphate, together with much pure fuming hydrochloric acid, added, and the arsenic distilled off as chloride (*cf.* p. 196). The filtrate from the copper sulphide is evaporated to drive off the sulphuretted hydrogen, cooled, and made up to 500 c.c. in a graduated flask. The nickel and cobalt from 100 c.c. of this solution (corresponding to 2 g.) are deposited on a cone electrolytically (p. 308), both metals weighed, the cobalt determined as tri-cobaltic tetroxide by Ilinski and von Knorre's method (p. 312), the solution from the nickel and cobalt filtered, and any magnesium present precipitated by the addition of a few drops of aqueous phosphoric acid. For the determination of the iron and manganese, the remaining 400 c.c. (corresponding to 8 g. of metal) are diluted with 1 to 2 litres of water, the solution warmed in a water-bath, a large excess of ammonia added, the cleared solution syphoned off after several hours, and the precipitate collected on an iron-free filter paper and washed for a short time. It is then dissolved in hot, dilute hydrochloric acid, the solution largely diluted, again precipitated with ammonia, redissolved in hydrochloric acid, the diluted solution saturated with ammonia in a porcelain dish, warmed, filtered, the precipitate washed, dried, strongly ignited in a weighed porcelain crucible with good access of air, and the mixture of oxides of iron and manganese weighed. The oxides are then dissolved in hydrochloric acid, the solution evaporated on the water-bath, and the residue taken up with a few drops of hydrochloric acid and water. The ferric chloride thus obtained may be titrated with stannous chloride, or the solution may be evaporated with sulphuric acid, diluted with water, reduced with zinc, and the ferrous sulphate titrated with potassium permanganate (*cf.* pp. 29 *et seq.*). The ferric oxide thus found is deducted from the weight of mixed oxides, and the difference is tri-manganic tetroxide. If much iron and manganese are present, they are separated by the sodium acetate method, the manganese precipitated in the filtrate as dioxide, the iron precipitate again dissolved in hydrochloric acid, precipitated with ammonia, and finally weighed as ferric oxide. The manganese is weighed as tri-manganic tetroxide.

*Determination of Sulphur.*—Ten grams are dissolved in pure nitric acid, the excess of acid evaporated off, twice evaporated to dryness with about 100 c.c. of pure hydrochloric acid, the residue taken up with hydrochloric acid and water, diluted to about 300 c.c., and the sulphur precipitated with barium chloride.

*Determination of Carbon.*—The carbon (together with the sand) remaining after dissolving 10 g. of nickel cubes in nitric acid is collected on an asbestos filter, washed, the filter transferred to a porcelain boat, dried, the carbon oxidised in a porcelain tube, and the carbon



dioxide absorbed in potash bulbs  $\text{CO}_2 \times \frac{3}{11} = \text{C}$ . On account of the small content of carbon, this determination is seldom carried out.

*Fused Nickel* (anode plates, granules) may contain several per cent. of carbon. Three grams of the finest possible drillings or granules are warmed in a beaker on a boiling water-bath with a concentrated solution of copper ammonium chloride (150 g.  $\text{NH}_4\text{Cl} \cdot \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  per 500 c.c.) for twenty-four to forty-eight hours, or until the nickel is completely dissolved, and the residue collected on an asbestos filter and washed, etc., as above. The determination of the small quantities of aluminium, calcium, and alkalis which occur in nickel cubes offers no difficulties, but is very lengthy, and is, therefore, not carried out for commercial analyses.

### 3. Metallic Cobalt.

The metal comes into commerce as cubes, and contains only very small quantities of impurities (nickel, iron, copper, carbon, sand); it is of no technical importance, and, on account of its high price, is seldom used for the preparation of alloys.

### 4. Nickel Alloys.

The alloys to be considered are chiefly those with copper, such as coinage alloys, *e.g.*, German, containing 75 per cent. of copper, and 25 per cent. of nickel, alloys for bullet envelopes, containing about 80 per cent. of copper and 20 per cent. of nickel, and those with copper and zinc, such as German silver, argentan, nickelin, etc.

*Analysis.*—One gram of drillings is dissolved in 10 to 15 c.c. of nitric acid (sp. gr. 1.2) in a covered porcelain dish on the water-bath, the solution evaporated with 5 c.c. of 50 per cent. sulphuric acid, any lead sulphate (from the spelter) which separates filtered off, and the copper in the filtrate deposited electrolytically in a crucible or dish, after the addition of nitric acid. If it is desired to precipitate the copper as sulphide by means of sulphuretted hydrogen, the filtrate from the lead sulphate is diluted to about 300 c.c. and 30 to 50 c.c. of hydrochloric acid (sp. gr. 1.124) added, so as to prevent the precipitation of zinc. If this addition is not made, the copper sulphide precipitate is first washed with hydrochloric acid to which some sulphuretted hydrogen water is added, and then with very dilute sulphuretted hydrogen water acidified with one drop of sulphuric acid. The filtrate is evaporated, the residual sulphate solution somewhat diluted, nearly neutralised with ammonia, diluted to 400 to 500 c.c., and sulphuretted hydrogen passed in for a considerable time (one to two hours) to precipitate the zinc as sulphide. The solution from the deposited copper is evaporated till the sulphuric acid begins to fume and thereby drives off all the nitric acid; the cooled residue is taken up with 100 c.c. of water, the solution neutralised in presence of a strip of Congo red paper until it just gives

a faint acid reaction, then largely diluted and the zinc precipitated with sulphuretted hydrogen (*cf.* pp. 288 *et seq.*). The zinc sulphide is filtered off after twelve hours, and washed with dilute sulphuretted hydrogen water containing several grams of ammonium sulphate. The filtrate, after the addition of 5 c.c. of sulphuric acid to prevent separation of nickel sulphide on evaporation, is evaporated in a porcelain dish to about 100 c.c., the cooled solution washed into a 200-c.c. beaker, 50 c.c. of strong ammonia added, the solution then cooled, and the nickel and cobalt deposited electrolytically on a conical cathode. The iron and manganese are filtered off from the solution after electrolysis, and separated and determined as described under the analysis of nickel (pp. 316 *et seq.*). Any hydrated manganese dioxide which adheres to the anode is removed by a glass rod, the end of which is covered with a piece of rubber tubing. A separation of nickel and cobalt is not necessary.

German silver and similar alloys frequently contain some tin (added to improve the colour of the metal), which is recognised on dissolving the alloy in nitric acid, diluting the solution, and boiling. It is determined as in the analysis of bronze (p. 208). Copper-nickel alloys, for parts of machinery, not unfrequently contain several per cent. of aluminium; in the analysis, the copper is first separated electrolytically, the nitric acid removed from the solution from the copper, excess of ammonia then added, and the nickel also deposited by electrolysis. The cloudy solution containing the aluminium hydroxide is then neutralised with acetic acid, diluted, boiled, the precipitate filtered off, washed, ignited, and the ferric oxide containing alumina weighed. The mixed oxides are fused in a platinum crucible with six times their weight of potassium hydrogen sulphate, the melt dissolved in hot, dilute sulphuric acid, the ferric sulphate reduced with zinc, and the iron titrated with potassium permanganate.

*Silver-plated German Silver.*—For the determination of the coating of silver, the well-cleaned articles (spoons, forks, etc.) are suspended by means of iron or platinum wires, connected to the positive pole of a battery, in a glass vessel filled with a 2 to 3 per cent. solution of potassium cyanide, and the silver deposited electrolytically on to a strip of thin copper foil, which serves as the cathode. The desilverised articles are removed from the bath, excess of hydrochloric acid added to the solution under a good fume cupboard on account of the evolution of hydrocyanic acid, and the solution evaporated so as to separate the silver as chloride; the copper foil, with the deposited silver, is dissolved in nitric acid, and the silver precipitated from the diluted solution with a slight excess of hydrochloric acid.

The removal of the layer of silver by means of nitric acid is not possible, since silver from the solution is always re-deposited on the

alloy. The scraping off of the silver with suitable instruments is very tedious and gives low results, since the "amalgamation" which precedes the silvering of German silvers rich in nickel eats somewhat deeper into the alloy than the electrolytically deposited silver. If the articles to be analysed may be destroyed, they can be completely dissolved in nitric acid, etc., or melted up in a crucible in a coke wind-furnace, an ingot cast and weighed, a weighed quantity of drillings from the ingot dissolved in nitric acid, and the silver determined in the resulting solution.

5. Iron-Nickel Alloys (Nickel Steel). (*Cf.* pp. 65 *et seq.*).

6. Determination of the Nickel on Nickel-plated Iron Articles.

The coating of nickel is dissolved off with hot, dilute nitric acid (one volume of acid of sp. gr. 1.2 to one volume of water), the solution evaporated to dryness, the evaporation repeated twice with hydrochloric acid, the nickel and iron separated by Rothe's method, and the nickel determined electrolytically.

7. Determination of Nickel in Nickel-plating Baths.

F. Lecoeuvre<sup>1</sup> titrates the nickel in the dilute ammoniacal solution with a 10 per cent. potassium cyanide solution (1 c.c. = 22 to 23 mg. Ni), which is standardised against a solution of pure nickel ammonium sulphate (containing 14.93 per cent. Ni). A measured volume of the nickel solution is introduced into a flask, made slightly alkaline with 5 per cent. ammonia, and the potassium cyanide solution run in from a burette, with continual agitation, until the solution suddenly clears and turns yellow. In the case of nickel-plating baths, which usually contain about 10 g. of nickel per litre, 100 c.c. are taken for the titration, and, according to Lecoeuvre, an accuracy of 0.02 g. in the litre is attainable. In baths which have been used for a long time and which are contaminated with iron, copper, zinc, etc., the nickel and impurities are determined by the usual gravimetric methods.

## MANGANESE

Of the numerous manganese ores proper, only the oxides are of technical importance, and of these more especially, *Pyrolusite*,  $\text{MnO}_2$ , and *Psilomelane*, according to Rammelsberg,  $\text{RO}_4\text{MnO}_2$  (in which  $\text{R} = \text{Mn}$ ,  $\text{Ba}$  and  $\text{K}_2$ ), which usually contain in addition some silica and small quantities of copper, cobalt, magnesium, and calcium. About nine-tenths of all the manganese ores and ores containing manganese are

<sup>1</sup> *Bull. Soc. Chim.*, 1895, 13, 1011; *J. Soc. Chem. Ind.*, 1896, 15, 135.



used in iron-smelting works for the manufacture of iron-manganese alloys such as spiegeleisen and ferro-manganese, whilst the remainder is used for the manufacture of chlorine, bleach, manganates, and permanganates, glass, the preparation of varnishes, etc., and to a small extent for the production of manganese-copper alloys.

The methods for the determination of manganese in manganese ores and iron ores containing manganese are fully described in the section on Iron (pp. 15 and 33). The most accurate gravimetric method of estimation is that of H. Rose, according to which it is determined as sulphide; on account of its lengthy character, it is only employed, however, when carrying out a complete analysis or as a deciding method. Of the volumetric methods, that of Volhard (p. 34) is the most generally used, and may be employed for the analysis of all substances containing manganese.

For the analysis of iron-manganese alloys, *cf.* Iron, p. 60. The analysis of manganese-copper alloys is described on p. 207 (Manganese Copper) and p. 208 (Manganese Bronze). The analytical methods for pyrolusite are described in Vol. I., pp. 476 *et seq.*

## CHROMIUM

*Chromite* or *Chrome iron ore* (approximating to the formula  $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$ ), which occurs in large quantities, forms the crude material from which all chromium compounds and chromium iron alloys are prepared. The mineral itself always contains more or less ferric oxide, alumina, and magnesia; the content of chromic oxide in the ore as it comes on to the market, varies between 30 and 62 per cent.

The valuation of the ore is usually effected by fusing a small quantity (0.35 to 0.5 g.) of the very finely ground substance with oxidising and fluxing agents, lixiviating the fusion with water, and titrating the chromic acid in the solution. In practically all the older methods of fusion some of the ore remained unattacked, and this had to be fused up again, which rendered the determination very tedious. This difficulty is entirely removed by the use of sodium peroxide, either alone or mixed with sodium hydroxide. The fusion methods of J. Spüller, S. Kalman, and of J. Lambert, described in the section on Iron, pp. 18-19, are applicable to all substances containing chromic oxide or chromium; the chromic acid in the solution, from which the excess of sodium peroxide is removed, is titrated by Schwarz's method (*cf.* Iron, p. 72).

J. Rothe<sup>1</sup> fuses 0.5 g. of the very finely powdered ore in a platinum crucible with four times the weight of a mixture of equal parts of nitre

<sup>1</sup> Private communication to Prof. Pufahl.

and previously dehydrated sodium hydroxide, heats to not above a dull red heat, and thus obtains complete decomposition of the substance.

The chromic acid in all soluble chromates is titrated by Schwarz's method, by acidifying with sulphuric acid, adding a weighed excess of ferrous ammonium sulphate, and titrating back the excess with potassium permanganate. Schwarz treats lead chromate by intimately rubbing it up with excess of ferrous ammonium sulphate and hydrochloric acid, adding a large quantity of water and titrating the solution with permanganate.

*Detection of Chromium.*—By fusing up the substance mixed with sodium carbonate in a small platinum spoon, or on a piece of foil or platinum wire, to a high temperature, and with good access of air, a yellow melt consisting of a chromate is produced, which, when dissolved in water, produces a yellow precipitate of lead chromate after the addition of acetic acid and lead acetate solution. Very minute quantities of chromium are recognised in iron and steel by the determination of the manganese by Hampe's chlorate method, the presence of chromium producing a yellow coloration in the filtrate from the manganese dioxide.

L. Duparc and A. Leuba have worked out the following method for the analysis of chrome iron ores<sup>1</sup>:—They discard the fusion with sodium peroxide, since crucibles of silver, platinum, or copper are thereby strongly attacked, as well as the fusion with acid potassium sulphate, which does not work well and is never quantitative, and substitute sodium carbonate in the following manner, which must be carried out accurately in every detail:—The mineral is ground exceptionally finely in an agate mortar, "bagged" through silk gauze, dried, not more than 0.2 to 0.3 g. mixed with 5 to 6 g. of pure sodium carbonate and heated for eight hours in a platinum crucible closed with the lid. Finally, the heat is increased and the crucible lid left half open. When the fusion is completed, the crucible is dipped into a porcelain dish containing 100 c.c. of cold water, in which it is allowed to remain for several hours. The contents of the crucible, washed out with water, are warmed on a water-bath with hydrochloric acid, so as to completely dissolve the suspended oxide of iron, the solution evaporated to dryness, again moistened with hydrochloric acid and again evaporated, this being repeated three times so as to separate the silica. The residue is finally taken up with dilute hydrochloric acid, the silica filtered off and estimated in the usual way. Ammonia is added in slight excess to the filtrate, and the solution warmed on the water-bath until the smell of ammonia is no longer recognisable. The precipitate contains the hydroxides of chromium, iron, and aluminium; it is filtered off, washed,

<sup>1</sup> *Chem. Zeit.*, 1904, 28, 518; *J. Chem. Soc. Abstr.*, 1904, 86, 592; and private communication to Prof. Pufahl.

dried, ignited in a platinum crucible, and the mixture of the three oxides weighed. Calcium and magnesium are estimated in the filtrate as usual. For the separation of the three oxides, the mixture is very finely ground, a portion weighed out, and again fused in a platinum crucible with sodium carbonate. On extraction with water, the iron remains as insoluble oxide, the chromium is dissolved quantitatively as sodium chromate and the aluminium as sodium aluminate. The solution is carefully neutralised with nitric acid, care being taken to avoid any excess of this acid, a slight excess of ammonia added, the excess driven off, the precipitated hydroxides dissolved in hydrochloric acid, the precipitation and dissolving repeated, the precipitate filtered off, washed (first with water containing sodium carbonate, then with pure water), and ignited, when perfectly pure white alumina is finally obtained. The chromate in the filtrate is reduced to chloride, and the chromium hydroxide precipitated with ammonia. If the slightest excess of nitric acid is used for the neutralisation of the solution, it reacts with the sodium chromate, to form a green hydroxide of aluminium containing chromium, which is precipitated on the addition of ammonia. Acetic acid reacts in a similar manner. Hydrochloric acid cannot be used on account of its reducing action on the chromate.

## TUNGSTEN<sup>1</sup>

Only two ores are employed as raw materials from which tungsten iron alloys and tungsten preparations are manufactured. *Wolframite*, consisting of isomorphous mixtures of  $\text{MnWO}_4$  and  $\text{FeWO}_4$ , containing 76 per cent. of tungstic acid, and *Scheelite*,  $\text{CaWO}_4$ , containing 80.5 per cent. of tungstic acid. Less important ores are *Tungstite*, or *Wolframite* ( $\text{WO}_3$ ), *Hubnerite* ( $\text{MnWO}_4$ ), *Stolzite* ( $\text{PbWO}_4$ ), and *Cupscheelite* ( $\text{CuCa}_2(\text{WO}_4)_3$ ).

For the determination of the contained tungstic acid, the very finely ground ore is decomposed by continued boiling with aqua regia or nitric acid, or it is fused in a platinum crucible with potassium sodium carbonate if it contains no arsenic (arsenical pyrites, etc.).

## METHODS OF ANALYSIS

### 1. Scheele's Method.

One to two grams of the very finely powdered mineral (wolframite or scheelite), dried at  $100^\circ$ , are repeatedly evaporated to dryness in a porcelain dish with an excess of hydrochloric acid, to which some nitric acid is finally added, and the residue is heated each time to about  $120^\circ$ .

<sup>1</sup> Cf. Gin, *Trans. Amer. Electrochem. Soc.*, 1908, 13, 522.



The final residue is then digested with hydrochloric acid and water, the tungstic acid, which is invariably contaminated with silica, filtered off, washed with hot water, washed off the filter paper into a beaker, dissolved in warm, dilute ammonia, the solution filtered through the same filter paper into a weighed platinum dish, the solution of ammonium tungstate evaporated, the residue completely dried, and finally converted by strong ignition into yellow tungstic acid.  $\text{WO}_3 \times 0.7931 = \text{Tungsten}$ .

## 2. Berzelius' Method.

One to two grams of the ore are fused in a nickel crucible with three to four times the weight of potassium sodium carbonate (the absence of arsenic and antimony is assumed), the cold melt extracted with hot water, the solution neutralised with nitric acid, the carbon dioxide expelled by warming, iron and alumina precipitated by means of ammonia, the solution again neutralised with nitric acid, then a cold saturated solution of mercurous nitrate added until no further precipitate is formed, and finally a few drops of ammonia added until the precipitate begins to turn brown. The precipitate is allowed to settle, filtered off, washed with water to which some of the mercurous nitrate solution is added, dried, and converted into tungstic acid by careful ignition in an open platinum crucible in the fume cupboard. By evaporating the residue with a few cubic centimetres of hydrofluoric acid and one drop of sulphuric acid, any silica carried down with the tungstic acid may be removed.

Wolframite containing tin-stone or arsenical pyrites is best treated according to method (1). For the determination of the tin in tungstic acid containing stannic acid, H. Talbot fuses the mixed oxides with six times their weight of potassium cyanide in a porcelain crucible for half an hour, dissolves the fusion in hot water, collects and weighs the metallic tin, and deducts the corresponding weight of stannic oxide from the weight of the impure tungstic acid.

## 3. Bullnheimer's Method.

This method<sup>1</sup> takes into special consideration the numerous minerals (scheelite, stolzite, tin-stone, arsenical pyrites, molybdenite, fluor-spar, bismuth, copper pyrites, quartz, mica, and other silicates) which accompany wolframite both in poor and in rich ores.

The determination of the tungsten is carried out as follows:—One to two grams of finely powdered ore is mixed in a nickel crucible with 4 g. of sodium peroxide, a small piece of sodium hydroxide (about 3 g.) placed in the mixture so that it rests on the bottom of the crucible, and then the crucible warmed over quite a small Bunsen flame until the

<sup>1</sup> *Chem. Zeit.*, 1900, 24, 870; *J. Chem. Soc. Abstr.*, 1901, 80, 41.

contents appear quite moist. The addition of sodium hydroxide serves to render the melt easily fluid, thereby making it easier to prevent portions of the ore settling and adhering to the bottom of the crucible. If this latter consideration is not attended to, the crucible soon becomes eaten into, whilst otherwise it can be used twenty times. The crucible is then heated with a larger flame, continually stirring with a nickel spatula, until the whole is quite liquid and the bottom of the crucible begins to glow. Wolframite is thus completely decomposed, whilst tin-stone is only partially attacked, and to some extent is left behind unchanged. After the fusion has solidified, the crucible and contents, whilst still hot, are placed in a beaker containing water; when the contents have dissolved, the solution is removed and washed into a 250 c.c. flask. If the solution is coloured green with manganate, hydrogen peroxide is added till discoloured. After cooling, the flask is filled up to the mark, half the solution filtered through a dry, folded paper, and 20 g. of ammonium nitrate added. When the latter is dissolved, the solution is allowed to stand quietly until the silica and stannic acid have settled, and then a sufficient quantity of magnesium nitrate solution is added, in small quantities at a time, with continual stirring, to precipitate any arsenic or phosphoric acids present.

The ammonium and magnesium salts used must be the nitrates, since chlorides or sulphates interfere with the subsequent precipitation with mercurous nitrate. After standing for from six to twelve hours, the precipitate is filtered off and washed, first with ammonia and then with water. It is essential to allow the silica and stannic oxide to settle before adding the magnesium nitrate, otherwise the precipitate easily carries some tungsten down with it. The ammoniacal solution is then made slightly acid with nitric acid, and after cooling, in case it has become very warm, 20 to 30 c.c. of mercurous nitrate solution added. The mercurous nitrate solution is prepared from 200 g. of mercurous nitrate, 20 c.c. of concentrated nitric acid, a little water, then warmed, and when dissolved, diluted to 1000 c.c. and kept over mercury. After several hours, ammonia is added until the solution has only a slight acid reaction; it is then allowed to stand until the liquid over the dark precipitate has cleared. The precipitate is then filtered off and thoroughly washed with water containing mercurous nitrate. By the foregoing procedure, the precipitate will be found to be retained completely by the filter paper, and the washings will also be perfectly clear. After drying, the filter paper is ignited, heated under the fume cupboard over a Bunsen burner, and then more strongly over a blow-pipe with access of air until of constant weight. If much molybdenum is present, which is seldom the case, its volatilisation is only complete after a considerable time. The same end is somewhat more quickly attained, if, after the first strong ignition, some ammonium chloride is

mixed with the contents of the crucible, which are then strongly ignited, first with the lid on and finally with the lid off.

#### 4. The Analysis of low-grade Wolfram Ores.

Hutchin and Tonks<sup>1</sup> have worked out the following method, which is specially suitable for the determination of tungstic acid in low-grade wolfram ores. About 5 g. or more, according to the richness of the sample, is weighed and digested in a porcelain dish with 20 c.c. of a 25 per cent. solution of sodium hydroxide (free from chloride) on a water-bath for thirty to forty-five minutes. After dilution, a little sodium peroxide is added to oxidise any decomposition products of sulphides and the solution diluted to 250 c.c. in a graduated flask; 200 c.c. are filtered through a dry filter paper, acidified with nitric acid, and then made alkaline with ammonia. The solution is then boiled, filtered, the precipitate washed, the filtrate made slightly acid with dilute nitric acid, and mercurous nitrate added in excess, followed by a few drops of dilute ammonia. On stirring and warming, the precipitate settles readily; it is filtered off, washed with a dilute solution of mercurous nitrate, the paper and precipitate ignited together in a porcelain crucible, or, if the ore be free from arsenic, in a platinum crucible, and weighed as tungstic acid.

#### 5. The Analysis of Tantaliferous Wolframite.<sup>2</sup>

The very finely pulverised mineral is treated with hydrochloric acid, to which a little nitric acid has been added, the whole boiled, then diluted with water, the clear solution decanted, and the residue washed by decantation. The insoluble residue is treated with ammonia and sulphuretted hydrogen, the solution decanted, and the residue washed with strong sulphuretted hydrogen water. The slight residue, coloured black by sulphide of iron, turns white on treatment with hydrochloric acid, and consists of a little unattacked wolframite and the tantalic acid. The hydrochloric acid solution obtained is added to that containing the iron, manganese, calcium, and magnesium. The decomposition of the original residue is completed by fusing with acid potassium sulphate, the fusion treated with boiling water, and the residue, after filtration, treated with ammonium sulphide, which takes up the rest of the tungsten.

The slight residue, coloured black by sulphide of iron, is purified by treatment with hydrochloric acid, which leaves the tantalic acid in an insoluble form combined with sulphuric acid; this is calcined at a bright red heat and the tantalum pentoxide weighed.

The combined ammonium sulphide solutions are evaporated to dry-

<sup>1</sup> *Trans. J. Min. and Met.*, 1908-9, 18, 425.

<sup>2</sup> *Gin, Trans. Amer. Electrochem. Soc.*, 1908, 13, 531.



ness, the residue moistened with a few drops of nitric acid, evaporated to dryness again, and strongly heated; the residual tungstic anhydride is then weighed.

The combined acid solutions are used for the estimation of the metals, iron and manganese being precipitated by means of ammonia and sulphuretted hydrogen, and the calcium, and magnesium estimated in the filtrate.

The methods of analysis applied to metallic tungsten and tungsten iron alloys are described under Iron, pp. 73 *et seq.*

## URANIUM

Uranium compounds (sodium and ammonium uranate) and uranyl nitrate, which are used in the manufacture of glass and for painting on porcelain, are for the greater part prepared from *Uranium pitch blende* (uranous-uranic oxide,  $U_3O_8$ ), which contains up to 80 per cent. intimately mixed with pyrites, arsenical pyrites, galena, etc., and which is found in Cornwall, at Joachimsthal, Johanngeorgenstadt, Adrianople, and other localities; and to a lesser extent from naturally occurring hydrated copper uranium and calcium uranium phosphates, such as copper uranite, calcium uranite, and uranium mica.

Poorer ores which come into commerce contain 30 to 60 per cent. of  $U_3O_8$ ; the *Uranium sands* of Carolina, Connecticut, and Colorado contain only from 8 to 18 per cent. Uranium minerals always contain the radio-active element radium, as well as helium.<sup>1</sup> Small amounts of compounds of copper, bismuth, silver, zinc, arsenic, and aluminium are also often present.

### METHODS OF ANALYSIS<sup>2</sup>

#### 1. H. Rose's Method.

About 1 g. of finely ground substance, dried at  $100^\circ$ , is warmed in a flask with 100 c.c. of strong nitric acid, the solution evaporated to dryness, the evaporation repeated with 20 c.c. of hydrochloric acid, the residue taken up with hydrochloric acid, 50 c.c. of a saturated aqueous solution of sulphur dioxide added, the solution warmed to reduce the arsenic oxide, boiled, and sulphuretted hydrogen passed in for some time after further dilution. The precipitate is filtered off, an excess of a cold, saturated solution of ammonium carbonate added to the filtrate, and then ammonium sulphide; zinc, iron, manganese, nickel, and cobalt separate as sulphides, whilst all the uranium remains in solution

<sup>1</sup> Cf. C. Baskerville, *Eng. and Min. J.*, 1909, 87, 257.

<sup>2</sup> A summary of the best methods of analysis are given by Kern, *J. Amer. Chem. Soc.*, 1901, 23, 685.

as uranous carbonate. When the precipitate of sulphides has settled, the supernatant liquid is poured through a filter paper, the precipitate repeatedly washed by decantation with water containing some ammonium sulphide and ammonium carbonate, after which the precipitate is brought on to the paper and thoroughly washed. The filtrate is boiled for some time, hydrochloric acid added to decompose the ammonium sulphide, again boiled for a quarter of an hour, and then the uranous oxide oxidised by boiling with a little nitric acid. All the uranium is now precipitated as hydroxide with a slight excess of ammonia, the precipitate washed with dilute ammonium chloride solution, dried, and, by igniting in a platinum crucible with good access of air, converted into the oxide  $U_3O_8$  ( $UO_2 \cdot 2UO_3$ ), which is weighed.  $U_3O_8 \times 0.8482 = \text{Uranium}$ . The amount of uranium in the ore is usually expressed in percentages of  $U_3O_8$ .

As a check on the estimation, the weighed oxide may be converted by strong ignition in a current of hydrogen into uranous oxide and weighed as such.  $UO_2 \times 0.8817 = \text{Uranium}$ .

## 2. A. Patera's Technical Assay.

One to five grams of the finely powdered ore are dissolved by heating for some time with a slight excess of nitric acid (sp. gr. 1.2), the solution diluted, excess of sodium carbonate solution added, boiled for a short time, the precipitate filtered off and washed with hot water. The filtrate contains all the uranium and only traces of other metals. It is neutralised with hydrochloric acid, the carbon dioxide expelled by boiling, orange coloured sodium uranate precipitated with sodium hydroxide, the precipitate filtered off, washed with a little hot water, and dried. The filter paper is ignited in a platinum crucible, the dried uranate added, the contents of the crucible strongly ignited, and, when cold, brought on to a small filter paper; the free alkali contained in the uranate is washed out with hot water, the filter paper and contents again dried, ignited, and the pure sodium uranate (uranium yellow) weighed. 100 parts  $Na_2U_2O_7 = 132.84$  parts  $U_3O_8$ .

According to C. Winkler, the results obtained in the analysis of ores rich in copper are somewhat too high, on account of a small amount of unprecipitated copper being carried over into the alkaline solution.

H. Bornträger<sup>1</sup> found that in the analysis of poor ores, and especially of uranium sands, considerable quantities of silica (up to 4 per cent.) are contained in the sodium uranate, and advises the dissolving of the uranium precipitate in hydrochloric acid, the filtering off of the silica, the precipitation of the uranium in the filtrate with ammonia, and finally weighing it as  $U_3O_8$  (*cf.* Method 1).

<sup>1</sup> *Z. anal. Chem.*, 1898, 37, 436; *J. Soc. Chem. Ind.*, 1898, 17, 1184.

### 3. Determination of Uranium in Ores containing Phosphorus and Arsenic (R. Fresenius and E. Hintz).<sup>1</sup>

The silica is separated as usual from the nitric acid, hydrochloric acid, or aqua regia solution, excess of potassium ferrocyanide added to the dilute hydrochloric acid solution, and the solution then saturated with sodium chloride. The precipitate, containing uranium, copper, and iron ferrocyanides, which soon settles, is first washed by decantation, and then on the filter paper with water containing sodium chloride, and is then treated with dilute potassium hydroxide without warming. When the decomposition of the ferrocyanides is complete and the hydrated oxides have settled, the solution is poured through a filter paper, the precipitate again washed once by decantation with water, and the hydrated oxides transferred to the filter paper with water containing ammonium chloride and ammonia, with which they are washed uninterruptedly until the filtrate, on acidifying, shows no traces of potassium ferrocyanide.

The hydrated oxides are then treated with hydrochloric acid. If the foregoing operations have been properly carried out, they are completely dissolved. Should an insoluble residue of ferrocyanides remain, after washing, it must be again treated with potassium hydroxide, etc., as described above.

The solution of metallic chlorides, which, if the precipitate of the ferrocyanides has been well washed, contains no phosphoric or arsenic acids, is concentrated; if necessary the greater part of the free acid is neutralised with ammonia, and to the clear solution a moderate excess of ammonium carbonate is added, and the solution allowed to stand for some time. The ferric hydroxide remaining undissolved is filtered off, washed with water containing some ammonium carbonate, the filtrate and washings heated so as to remove the greater part of the ammonium carbonate, the solution acidified with hydrochloric acid, whereby the yellow flocculent precipitate containing some of the uranium and which was produced by boiling, is redissolved, and sulphuretted hydrogen then passed in to the hot solution to precipitate the copper. The copper sulphide is always obtained free from uranium. The filtrate from the copper sulphide is concentrated, and the uranium precipitated with ammonia as hydrated uranium oxide, which is converted by igniting in an open crucible into uranous uranic oxide, and weighed as such. As a check, the contents of the crucible are ignited in a current of hydrogen and the weight of uranous oxide also obtained.

According to published results, the method is to be recommended; it is specially suited to the analysis of ores containing uranium mica (phosphate) and uranium arsenate.

<sup>1</sup> *Z. anal. Chem.*, 1895, 34, 437; *J. Chem. Soc. Abstr.*, 1895, 68, 536; cf. also E. F. Kern, *J. Amer. Chem. Soc.*, 1901, 23, 685; *J. Soc. Chem. Ind.*, 1901, 20, 1144.



#### 4. Analysis of Uranium-Vanadium Ores (*Carnotite*).

The details of analysis are described under Vanadium, p. 338.

#### 5. Uranium Yellow.

Fritchle<sup>1</sup> has published a method for the analysis of uranium, and vanadium ores, in which the reduced solutions of uranium and vanadium are titrated with permanganate.

The uranium yellow of commerce, which is practically chemically pure sodium uranate, is valued, according to Schertel,<sup>2</sup> chiefly by its appearance in comparison with recognised good samples. It should dissolve in hydrochloric acid without leaving any residue. If the clear solution is neutralised with ammonia, excess of ammonium carbonate added, and the solution warmed, no cloudiness should be produced. A drop of ammonium sulphide solution added to this solution should produce no precipitate, but only a dark coloration.

### VANADIUM

Vanadium is very widely diffused although in inconsiderable quantities. It is found in many silicate rocks, particularly in those rich in magnesium and iron, also in clays, bauxites, in many oolitic brown hæmatites, and even in lignites. The extraordinarily high percentage of 38.5 per cent. of vanadic acid has been found in the ash of a lignite from San Rafael, Province Mendoza, Argentine.

The demand for vanadium has very greatly increased since its recent application in the manufacture of special steels. Of late years numerous new sources of the metal, in workable quantities, have been discovered.

*Vanadium Ores*.<sup>3</sup>—The best known ores with a high content of the metal are: *Vanadinite*,  $3\text{Pb}_3(\text{VO}_4)_2 \cdot \text{PbCl}_2$ , containing up to 19.3 per cent. of vanadium pentoxide, and *Descloizite* (often found associated with vanadinite), a hydrated lead zinc vanadate with up to 22.7 per cent. of vanadium pentoxide. Important recent sources of the metal are: *Mottramite*, a hydrated lead copper vanadate containing up to 18.8 per cent. of vanadium pentoxide; *Roscoelite*, or *Vanadium mica*, containing up to 24 per cent. of vanadium pentoxide; *Carnotite*, a hydrated potassium uranium vanadate with 15 to 18 per cent. of vanadium pentoxide; *Patronite*,<sup>4</sup> a mixture of vanadium sulphide with molyb-

<sup>1</sup> *Eng. and Min. J.*, 1900, 70, 548.

<sup>2</sup> Cf. Post, *Chemisch-technische Analyse*, 3rd ed., Vol. I., p. 792.

<sup>3</sup> Cf. Katzer, *Osterr. Z. f. Berg-u.-Hüttenwesen*, 1909, 57, 411.

<sup>4</sup> Cf. D. F. Hewett, *Bull. Amer. Inst. Min. Eng.*, 1909, p. 291; *J. Iron and Steel Inst.*, 1909, 80, 337.

denum trioxide, silica, alumina, and oxides of iron, etc., containing up to 10 per cent. of vanadium; and *Anthracite* (*Asphaltite*) rich in sulphur, which occurs in the Quisque and Yauli districts in Peru, and contains up to 1.5 per cent. of vanadium pentoxide. All these raw materials, including the above-mentioned ashes of lignites, serve for the manufacture of vanadium preparations, chiefly ferro-vanadium. This alloy comes on the market with a content of up to 34 per cent. of vanadium, and may be obtained, either free from, or containing carbon.

### Detection of Vanadium in Rocks, etc. (W. Hillebrand).<sup>1</sup>

Five grams of the finely pulverised mineral are fused over the blowpipe with a mixture of 20 g. of sodium carbonate and 3 g. of sodium nitrate. The mass is extracted with hot water, some alcohol added to reduce any manganate formed, the solution filtered, the filtrate almost neutralised with nitric acid (the necessary quantity of the acid is found by a blank experiment), evaporated nearly to dryness, taken up with water, and filtered. The filtrate, which must be alkaline, is mixed with mercurous nitrate solution, which may cause a precipitate of mercurous phosphate, arsenate, chromate, molybdate, tungstate, and vanadate, as well as of much basic mercurous carbonate. The liquid is boiled, filtered, the precipitate dried, detached from the filter paper, and heated in a platinum crucible in a draught cupboard. The residue is ignited and fused with a very small quantity of sodium carbonate and extracted with water; a yellow colour of the solution indicates the presence of chromium. The solution is acidified with sulphuric acid, and traces of platinum, molybdenum, and arsenic, precipitated by sulphuretted hydrogen in a pressure bottle; the precipitate is filtered off, the sulphuretted hydrogen boiled off, the filtrate evaporated down until almost all the sulphuric acid is expelled, and the residue dissolved in 2 or 3 c.c. of water; a few drops of hydrogen peroxide solution are then added, when a brownish yellow coloration shows the presence of vanadium.

In order to detect vanadic acid in the presence of chromic acid, E. Champagne<sup>2</sup> recommends shaking the solution, which has been acidified with sulphuric acid, with hydrogen peroxide and ether. A blue coloration of the ethereal layer indicates chromium, while a yellow coloration (brownish yellow if considerable quantities are present) of the aqueous solution shows the presence of vanadium.

### Detection of Vanadium in Iron Ores, etc. (Lindemann).<sup>3</sup>

A few grams of the very finely powdered ore and four times the quantity of fusion mixture are fused for half an hour either in a red-hot

<sup>1</sup> *J. Amer. Chem. Soc.*, 1898, 20, 209; *Chem. News*, 1898, 78, 216; Treadwell and Hall, *Analytical Chemistry*, vol. i., p. 436.

<sup>2</sup> *Ber.*, 1903, 36, 3164.

<sup>3</sup> *Z. anal. Chem.*, 1879, 18, 102.

muffle or over the blowpipe. The melt is extracted with water, silica separated by adding excess of hydrochloric acid and evaporating, the residue taken up with hydrochloric acid and water, the solution filtered, saturated at 60° to 70° with sulphuretted hydrogen, and allowed to stand for twenty-four hours in a moderately warm place. The time may be shortened by the use of a pressure bottle. The filtrate, which in presence of vanadium is more or less distinctly blue in colour, is boiled to remove sulphuretted hydrogen, and concentrated to a small volume. The oxidation of vanadium tetroxide to pentoxide is then effected by adding a few crystals of potassium chlorate. Chlorine is driven off by further evaporation, the solution allowed to cool, and any salts which separate out dissolved by adding water; a slight excess of ammonia is then added to combine with any trace of free chlorine, and the solution faintly acidified with sulphuric acid. The vanadic acid thus formed may, if desired, be then titrated with standardised ferrous sulphate solution, using potassium ferrocyanide as indicator (*cf.* the volumetric estimation of vanadium, p. 335). For quantitative estimations, Lindemann fuses the residue again with fusion mixture and potassium nitrate.

#### METHODS OF ANALYSIS<sup>1</sup>

##### A. GRAVIMETRIC METHODS

###### Estimation of Vanadium as Vanadium pentoxide.

This method is seldom used. If vanadic acid has been precipitated as pure mercurous vanadate (H. Rose, p. 337) from a nitric acid solution which is free from arsenic, molybdenum, tungsten, chromium, and phosphorus, the precipitate can be converted by moderate ignition into brownish red vanadium pentoxide, which is just melted at a higher temperature in order to complete the expulsion of mercury, and then solidifies to a crystalline mass. From pure, alkali-free ammonium vanadate, analytically pure vanadium pentoxide, with 56.14 per cent. of vanadium, can be obtained by prolonged ignition with access of air. Any tungstic acid contained in the vanadic acid solution can be removed by repeatedly evaporating to dryness with hydrochloric or nitric acid; vanadium pentoxide (reduced to tetroxide by hydrochloric acid) is readily soluble in the dilute acids. Arsenic and molybdenum are separated in the hydrochloric acid solution by prolonged treatment with sulphuretted hydrogen and heating in a pressure bottle. Any phosphoric acid present is precipitated as mercurous salt and is left as phosphorus pentoxide mixed with the vanadium pentoxide; in this

<sup>1</sup> *Cf.* Treadwell and Hall, *Analytical Chemistry*, vol. ii., 1910, p. 273; A. Classen, *Ausgewählte Methoden d. anal. Chemie*, i., p. 230; Muspratt's *Handbuch der technischen Chemie*, 4th ed., 1905, p. 1742.



case the residue sinters but does not melt. The impure precipitate is fused with sodium carbonate, the solution acidified with sulphuric acid, and, after reducing the vanadium pentoxide to vanadyl sulphate, the phosphoric acid is estimated by ammonium molybdate solution and the quantity found subtracted. The presence of chromium is recognised by the colour of the solution obtained on extracting the residue after fusion with sodium carbonate and potassium nitrate; this recognition is facilitated by first decomposing any manganate present with alcohol, and then filtering. Vanadium is estimated volumetrically, according to Lindemann's method, which is not affected by the presence of chromic salts.

According to Roscoe, vanadic acid can be precipitated quantitatively as orange-yellow lead vanadate from a vanadate solution slightly acidified by acetic acid. Since the precipitate has not a constant composition, it is advisable, after washing, to decompose it with sulphuric acid, filter off the lead sulphate, and to titrate the vanadium in the filtrate, after reducing the pentoxide to the tetroxide. The lead vanadate may also be decomposed with hydrochloric acid, the lead chloride dissolved in hot water, sulphuretted hydrogen passed through the diluted solution, the lead sulphide filtered off, and the vanadium tetroxide contained in the filtrate titrated after boiling off the sulphuretted hydrogen.

In all cases it is advisable to fuse the weighed vanadic acid with sodium carbonate, and, after adding excess of sulphuric acid to the aqueous solution of the fused mass, to reduce it to the tetroxide, and then to check the gravimetric result by a volumetric estimation.

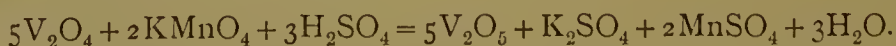
## B. VOLUMETRIC METHODS

These methods are most frequently employed, and are both rapid and very accurate.

### 1. Titration of Vanadyl sulphate with Potassium permanganate.

Vanadic acid in a solution acidified with sulphuric acid is at once reduced to the tetroxide by sulphuretted hydrogen, and by sulphur dioxide. After boiling off the reducing agent, the dilute bluish solution, which should be at a temperature of about 70°, is titrated with dilute permanganate, whereby re-oxidation to the pentoxide occurs.

The end-point is shown by a reddish coloration. The reaction is represented by the following equation:—



The iron value of the permanganate solution, multiplied by 1.632, gives the vanadium pentoxide, or, multiplied by 0.916, the vanadium.

The vanadium solution should contain from 0.1 to 0.2 g. of the

pentoxide and a few cubic centimetres of sulphuric acid in 500 c.c. The solution is mixed with about 30 c.c. of freshly prepared, saturated sulphurous acid solution, warmed, boiled, and the removal of the sulphur dioxide accelerated by passing in carbon dioxide. After boiling for half an hour, the escaping gases are tested for sulphur dioxide by passing them through a test tube of water rendered faintly pink by permanganate, which should not be decolorised (Treadwell). The reaction with starch iodide paper is less sensitive.

Hillebrand and Ransome (*cf.* *Ore Analysis*, I (b), p. 338) have observed that old solutions of sulphur dioxide in water, and also solutions of alkali sulphites, contain other oxidisable substances besides sulphur dioxide, which are not removed from the solution acidified with sulphuric acid even by prolonged boiling.

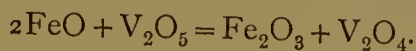
Sulphuretted hydrogen is not usually employed as the reducing agent; the filtrate from the copper, lead, and arsenic precipitate obtained in the course of the analysis can, however, be titrated with permanganate after boiling off the sulphuretted hydrogen (*cf.* *Ore Analysis*, I (b)). The titration can be repeated after passing sulphur dioxide through the solution, which has been cooled after titration (or a fresh addition of aqueous sulphurous acid can be made), and boiling off the excess.

The vanadium value of the permanganate solution may be determined directly by means of a pure preparation of vanadium pentoxide, such as ammonium vanadate which has been purified by recrystallisation. The vanadium pentoxide content is determined by careful heating, ignition, and fusion of about 0.5 g. Approximately 0.2 g. of the preparation (containing about 76.7 per cent. of vanadium pentoxide) is then weighed out, dissolved in hot water with addition of sulphuric acid, and the estimation carried out as described above.

This method gives excellent results.

## 2. Titration of Vanadic acid with Ferrous sulphate (Lindemann).

Lindemann (*cf.* p. 332, *Detection of Vanadium*) reduces the pentoxide to tetroxide in a cold solution, slightly acidified with sulphuric acid, with a solution of ferrous sulphate (or ferrous ammonium sulphate) which has been recently standardised by permanganate; potassium ferricyanide solution is used as the indicator. The reduction takes place in accordance with the equation:—



Hence 55.88 parts of ferrous iron correspond to 51.2 parts of vanadium.

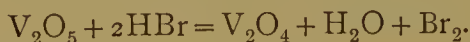
The solution of vanadic acid, oxidised exactly according to Lindemann's directions, is diluted to 300 c.c., and one-third of the solution used

in a preliminary experiment to determine the approximate volume of ferrous sulphate solution required. The titration is repeated with half of the remaining solution, and the residual third is used for a control estimation. Chromium contained in the original substance is finally present as chromic chloride, which is not altered by permanganate. A special advantage of this method is, that ferric iron may be contained in the pentoxide solution.

In the analysis of an ore (*cf.* H. Rose's method, p. 337), for instance, the percentage of vanadic acid can be accurately determined in presence of the generally small quantity of iron, in the solution obtained by decomposition with hydrochloric acid or aqua regia which has been freed from lead, copper, arsenic, and molybdenum by sulphuretted hydrogen, and the filtrate evaporated down and oxidised with potassium chlorate. In the titration with permanganate (method **I**), on the other hand, the ferrous salt present is titrated as well, and an iron estimation is required to correct the result. Since, in the separation of iron and vanadium, repeated treatment with alkali hydroxide is necessary in order to obtain vanadium-free ferric hydroxide, this applicability of Lindemann's method is especially valuable.

### 3. Iodometric estimation of Vanadium (Holzverscheidt).<sup>1</sup>

When ores and compounds containing vanadium pentoxide are treated with hot hydrochloric acid, chlorine is evolved, but the percentage of pentoxide present cannot be calculated from the amount of chlorine liberated, because the reduction of the pentoxide to the lower oxides proceeds differently, according to the concentrations of the acid and of the pentoxide solution. In presence of potassium bromide, however, the reduction proceeds quantitatively in accordance with the equation:—



To carry out the estimation, 0.3 to 0.5 g. of the vanadate and 1.5 to 2 g. of potassium bromide are introduced into a Bunsen flask as used for the analysis of pyrolusite, 30 c.c. of concentrated hydrochloric acid added, the whole boiled, and the evolved gases led into a potassium iodide solution placed in the receiver. The liberated iodine is then titrated with *N*/10 sodium thiosulphate, of which 1 c.c. = 0.00912 g.  $\text{V}_2\text{O}_5$ .

The method gives excellent results, and is especially suitable for the examination and valuation of vanadic acid preparations and of vanadates free from iron.

<sup>1</sup> Dissertation: Berlin, 1890; Treadwell and Hall, *Analytical Chemistry*, 1910, vol. ii., p. 622.



## C. ESTIMATION OF VANADIUM IN ORES

## 1. Estimation of Vanadium in Vanadium Ores (Vanadinite, Descloizite, Cupro-descloizite, Mottramite, etc.).

(a) *H. Rose's Method*.—This method consists in the separation of the vanadic acid by means of mercurous nitrate solution, and then weighing the pure pentoxide derived from the precipitate.

To carry out the determination, 1 g. of a finely powdered average sample is decomposed with 20 c.c. of ordinary hydrochloric acid in a covered basin, the solution evaporated down, taken up with a little hydrochloric acid and much hot water, the volume made up to about 500 c.c., and sulphuretted hydrogen passed in for one to two hours. To separate arsenic completely, the beaker containing the solution is then heated in a boiling water-bath, again treated for half an hour with sulphuretted hydrogen, and, after standing for some time (best over night), filtered into a capacious porcelain basin; the precipitate of lead, copper, and arsenic sulphides is washed with water containing hydrochloric acid and sulphuretted hydrogen. The filtrate is first evaporated over a flame, without boiling, and then on the water-bath; 20 c.c. of ordinary nitric acid are poured on to the solid residue and evaporated, at first under a watch-glass on account of spirting. This evaporation with nitric acid is then repeated once or twice in order to remove all the chlorine. The residue is taken up with the smallest possible quantity of nitric acid and with hot water, and heated in a basin (preferably platinum) with an excess of pure sodium hydroxide solution; the ferric hydroxide precipitate is filtered off, washed with hot water, dissolved in a little nitric acid, again treated with excess of pure sodium hydroxide, filtered, and washed. (If there is a considerable percentage of iron in the ore, the precipitate should be redissolved and the above treatment repeated). The united filtrates and washings are then saturated with carbon dioxide, gently warmed, and filtered from any separated alumina and zinc carbonate, etc. Nitric acid in slight excess is added to the filtrate, contained in a large covered beaker, and the carbon dioxide completely removed by boiling. The liquid is then allowed to cool, mixed with 10 c.c. of a cold, saturated solution of mercurous nitrate, stirred, then neutralised with ammonia, and the voluminous greyish brown precipitate (which contains all the vanadium as mercurous vanadate) filtered, and washed carefully with water containing 1 c.c. of saturated mercurous nitrate solution per litre, until the filtrate no longer gives a distinct sodium reaction.

After drying, the precipitate and filter paper are gradually heated in a platinum crucible, in the draught cupboard, the filter carbonised, the lid removed, and the crucible gently ignited over a small flame until the

carbon is completely burnt; the flame is then increased and the vanadic acid fused at a red heat.  $V_2O_5 \times 0.5614 = \text{Vanadium}$ .

The expulsion of the carbon dioxide is necessary, or otherwise much mercurous carbonate is contained in the precipitate. The mercurous nitrate solution is prepared by warming ordinary nitric acid with excess of mercury, and keeping the solution over mercury. Since the solution to be precipitated contains a large quantity of sodium nitrate, considerable dilution is advisable. In case a control is necessary, the weighed vanadic acid is fused with potassium and sodium carbonates, the fused mass dissolved in water, excess of sulphuric acid added, and the vanadic acid in the solution estimated volumetrically after conversion into the tetroxide.

(b) *W. Hillebrand and F. L. Ransome's Method*.<sup>1</sup>—One gram of the very fine powder is carefully fused in a platinum crucible with 4 g. of sodium carbonate (or fusion mixture) and the fused mass extracted with hot water. The residue is washed with hot water on a filter, which is dried and ignited. The fusion is repeated on account of the considerable quantity of vanadic acid which is retained in the undissolved residue. The united filtrates are acidified with sulphuric acid, heated almost to boiling, and sulphuretted hydrogen passed in for a long time, which precipitates the arsenic and any molybdenum present and reduces the vanadic acid to the tetroxide ( $V_2O_4$ ). The precipitate is filtered and washed thoroughly with water containing sulphuretted hydrogen. The filtrate, amounting to about 500 c.c., is boiled in a flask for half an hour, while carbon dioxide is passed in, until it is free from sulphuretted hydrogen. The vanadium tetroxide is then titrated in the hot solution with moderately concentrated permanganate until a permanent coloration is produced. The resulting vanadic acid is reduced by passing sulphur dioxide into the cooled solution, the excess of the gas completely removed by boiling, and finally by passing carbon dioxide, and again titrated with permanganate. The result now obtained is usually somewhat lower, but is assumed to be correct. (Cf. p. 334, *The Volumetric Estimation of Vanadium by Permanganate*.)

Any uranium contained in the ore does not influence the result, because it remains in the residue as sodium uranate. Pufahl prefers to add 1 g. of potassium nitrate to the mixture, and to fuse in a porcelain crucible over a large Bunsen burner; fusion in a muffle is not advisable, as the mass readily froths over.

## 2. Analysis of Uranium-Vanadium Ores (Carnotite, etc.).

(a) *Fritchle's Method*.<sup>2</sup>—Half a gram of the very finely powdered ore is heated for an hour with 20 c.c. of nitric acid in a 200 c.c. flask; 10 c.c.

<sup>1</sup> *Amer. J. Science*, 1900, 10, 120; *J. Soc. Chem. Ind.*, 1900, 19, 937. U.S. Geological Survey, Bulletin 176; cf. also, Low, *Technical Methods of Ore Analysis*, 1905, p. 203.

<sup>2</sup> *Eng. and Min. J.*, 1900, 70, 548.

of water are then added, the solution neutralised with a saturated sodium carbonate solution, a further quantity of 5 c.c. of sodium carbonate solution and 20 c.c. of a 20 per cent. sodium hydroxide solution added, and the solution boiled for half an hour. Sodium carbonate precipitates the uranium, vanadium, and iron, but the vanadium pentoxide dissolves again in the sodium hydroxide solution. The precipitate is filtered off and washed with dilute sodium hydroxide solution until the filtrate gives no vanadium reaction. The residue is dissolved in 20 c.c. of dilute nitric acid (1 : 1), diluted with 40 c.c. of water, neutralised with ammonia, 40 c.c. of saturated ammonium carbonate solution added, and the solution heated but not boiled. Ferric hydroxide is precipitated, whilst the uranium remains in solution. The precipitate is filtered off, washed thoroughly with 2 per cent. ammonium carbonate solution, and an excess of dilute sulphuric acid added to the filtrate, which is then evaporated until sulphuric acid fumes begin to be evolved. After cooling, the residue is taken up with 100 c.c. of water and reduced by boiling for half an hour with strips of aluminium. The uranium is titrated in the solution with a permanganate solution which has been standardised against iron. The iron value of the permanganate, multiplied by 2.133, gives the uranium, or, multiplied by 2.5167, the uranoso-uranic oxide,  $U_3O_8$ . The iron oxide residue is dissolved in dilute sulphuric acid, reduced with aluminium, and titrated with the same permanganate solution.

For the estimation of the vanadium, 0.5 g. of the ore are dissolved in 10 c.c. of nitric acid, 10 c.c. of sulphuric acid added, and the solution boiled until sulphuric acid fumes appear. After cooling, water is added, the iron, vanadium, and uranium reduced with aluminium and titrated together, with permanganate, which causes the solution to change its colour through purple-blue, blue, green, and yellow, to pink.

The volume of permanganate equivalent to the iron and uranium previously titrated is subtracted, and the difference represents that required for the oxidation of the vanadium tetroxide to pentoxide. (*Cf.* The Volumetric Estimation of Vanadium, method I, p. 334.)

This method is very satisfactory, but the precipitations must be repeated when the ore contains a notable quantity of iron, and the aluminium used for the reductions must be free from iron.

(*b*) *A. N. Finn's Method (for Carnotite)*.<sup>1</sup>—A quantity of the average sample which does not contain more than 0.25 g. of uranoso-uranic oxide,  $U_3O_8$ , is weighed out, decomposed with hot sulphuric acid (1 : 5), and the solution evaporated until fumes of the acid begin to be evolved. After cooling, the residue is taken up with water and boiled with an excess of sodium carbonate solution until the precipitate settles well. The precipitate is filtered off, washed, dissolved in the smallest possible

<sup>1</sup> *J. Amer. Chem. Soc.*, 1906, 28, 1443.



quantity of dilute sulphuric acid, and again precipitated. The united filtrates and washings are acidified with sulphuric acid, 0.5 g. of ammonium phosphate added, boiled, made alkaline with ammonia, boiled again for a few minutes, and the precipitate of ammonium uranyl phosphate, which contains all the uranium, washed with hot water containing some ammonium sulphate.

The vanadium is titrated in the filtrate, with permanganate, after acidifying with sulphuric acid, followed by treatment with sulphur dioxide and removal of the excess by boiling, as described above.

The uranium precipitate is dissolved in sulphuric acid, an ample quantity of granulated zinc added, and the reduction allowed to proceed for half an hour; the solution is then filtered on the pump through an asbestos filter to separate zinc (and finely divided lead), and the uranyl sulphate solution warmed to about  $60^{\circ}$  and titrated with  $N/20$  permanganate.<sup>1</sup> The percentage of uranium or of uranic oxide is calculated from the iron value of the permanganate solution as in Fritchle's method.

(c) *Method of Ledoux & Co.*<sup>2</sup>—One gram of the ore, previously finely powdered and dried at  $100^{\circ}$ , is gently heated in a small beaker with 25 c.c. of dilute nitric acid (1 : 3), the solution filtered, and the residue washed with hot water. The filtrate is diluted, the lead, copper, etc., precipitated by sulphuretted hydrogen, the solution filtered, and the filtrate boiled to remove the excess of sulphuretted hydrogen. Hydrogen peroxide is then added to oxidise the iron and vanadium, and the excess decomposed by boiling. The solution, which contains all the uranium and vanadium, is allowed to cool, neutralised with ammonia, an ample quantity of saturated ammonium carbonate solution added, and, after heating gently for a quarter of an hour, the ferric hydroxide precipitate filtered off. Since this precipitate retains some uranium and still more vanadium, it is dissolved in the smallest possible quantity of dilute nitric acid and reprecipitated. If it still gives the vanadium reaction when a few drops of hydrogen peroxide are added to its solution in nitric acid, the precipitation must be repeated once more. The united filtrates and washings are boiled in a large beaker to remove ammonia and ammonium carbonate, the solution finally becoming turbid by separation of uranium and vanadium compounds; this turbidity is removed by adding nitric acid, drop by drop, to the boiling solution. The beaker is then removed from the flame, 10 c.c. of a cold, saturated solution of lead acetate and a few grams of sodium acetate immediately added in order to completely precipitate the lead vanadate. The heating is continued for a short time on the water-bath until the precipitate has settled, when it is filtered off and washed with hot water slightly acidified with

<sup>1</sup> Bělohonbek's method, *Z. anal. Chem.*, 1872, **11**, 179.

<sup>2</sup> A. H. Low, *Technical Methods of Ore Analysis*, 1905, p. 204.

acetic acid. No vanadium is contained in the filtrate, but the lead vanadate may retain some uranium. The precipitate is washed from the filter paper into a beaker, and dissolved, together with the residue on the filter paper, in the smallest possible quantity of nitric acid, the solution diluted, a few cubic centimetres of lead acetate solution and a sufficient quantity of sodium acetate (5 to 10 g.) added, and the lead vanadate, now free from uranium, filtered off. The filtrate is united with that first obtained and kept for the determination of the uranium.

For the estimation of the vanadium, the lead vanadate is dissolved in nitric acid (*cf.* also p. 334, Roscoe's method), and the lead removed from the solution by adding excess of sulphuric acid and filtering. The filtrate is boiled down in a flask until the sulphuric acid is evaporated off, taken up with water, sulphur dioxide passed in, the excess boiled off, and the vanadium tetroxide titrated with permanganate. (*Cf.* The Volumetric Estimation of Vanadium, p. 334.)

To the solution kept for the estimation of uranium, 10 c.c. of concentrated sulphuric acid are added, and the lead sulphate filtered off. The filtrate is made slightly alkaline with ammonia, boiled, the ammonium uranate which settles collected on a filter paper, and, without washing the precipitate, dissolved at once in dilute sulphuric acid (1 : 6). The solution is boiled down in a flask until sulphuric acid fumes begin to be evolved, and finally, after reduction with zinc (*cf.* Finn's method, p. 339), the uranyl sulphate is titrated with permanganate by Bélohonbek's method (p. 340).

### 3. Estimation of Vanadium in Furnace-pigs.<sup>1</sup>

A few grams are decomposed by moderately heating in a current of chlorine, whereby vanadium chloride, as well as molybdenum and some iron, pass over into the water in the receiver. Molybdenum is removed from the solution by sulphuretted hydrogen, and iron by ammonium sulphide. The vanadium is then precipitated from the filtrate as sulphide on adding acetic acid, and converted into the pentoxide by heating in the air.

### 4. Estimation of Vanadium in Slags.<sup>2</sup>

Four grams of the very finely powdered slag (from the Bessemer treatment of pig iron containing vanadium) are decomposed in a few minutes by boiling with 60 c.c. of dilute sulphuric acid (1 : 4). After cooling, the solution is diluted to 80 c.c., and all the iron and vanadium oxidised by the addition of 40 c.c. of *N*/10 permanganate. The excess of permanganate is just removed by dropping in a very dilute ferrous sulphate solution, and the vanadium pentoxide then titrated by Lindemann's method (p. 335).

<sup>1</sup> A. Classen, *Ausgewählte Methoden der anal. Chemie*, 1901, vol. i., p. 235.

<sup>2</sup> C. H. Ridsdale, *J. Soc. Chem. Ind.*, 1888, 7, 73.

The estimation of vanadium in pig iron, steel, and ferro-vanadium is described in the section on "Iron," p. 75.

## MOLYBDENUM

The most commonly occurring minerals used for the manufacture of molybdenum preparations, as well as for the metal itself recently employed for special steels, and for the alloy with iron (ferro-molybdenum) are:—*Molybdenite*,  $\text{MoS}_2$ , and *Wulfenite*,  $\text{PbMoO}_4$ . The following minerals occur to a more limited extent:—*Molybdite*,  $\text{MoO}_3$ ; *Ilsemanite*,  $\text{Mo}_3\text{O}_8$ ; *Molybdurane*,  $\text{UO}_2 \cdot \text{UO}_3 \cdot 2\text{MoO}_4$ ; *Molybdoferrite*,  $\text{FeMoO}_4$ ; *Peteraite*,  $\text{FeCoMo}_2\text{O}_8$ ; *Eosite*,  $\text{Pb}_3\text{V}_2\text{MoO}_{16}$ . The slags of the Mansfeld Copper Works also contain a considerable proportion of molybdenum.

## METHODS OF ANALYSIS

The following are some of the analytical methods for molybdenite and wulfenite, which have been proved to be satisfactory:—

### I. Estimation of Molybdenum in Molybdenite.

(a) *A. Gilbert's Method*.<sup>1</sup>—In this method the ore is roasted with access of air, dissolved in ammonia, and filtered. The very small quantity of molybdenum left in the residue, probably as molybdate, is rendered soluble by fusion with sodium carbonate, reduced to the oxide,  $\text{Mo}_2\text{O}_3$ , by zinc in presence of an excess of hydrochloric acid, and titrated with permanganate.

To carry out the estimation, 1 g. of the very finely powdered substance is weighed into a porcelain boat, which is placed in the middle of a combustion tube 60 to 70 cm. in length. The tube is slightly inclined, and the middle portion is surrounded by tiles and heated by two powerful Bunsen flames. After three to four hours, the ore is completely roasted; only a very small quantity of a sublimate of molybdenum trioxide forms inside the tube. When the tube is cold, the boat is transferred with the aid of a long wire to a large beaker, and treated with not too dilute ammonia, in which the molybdenum trioxide dissolves completely after digesting for from two to three hours. The trace of the trioxide attached to the tube is carefully loosened, and the tube washed with ammonia, which is added to the bulk of the solution. When all the trioxide is dissolved, the solution is filtered, and the filtrate cautiously evaporated down in a large platinum basin; the basin is then covered by the lid, and the dry residue heated to constant weight over a rose-burner. The whole of the ammonia is easily driven off, and all the molybdenum is converted into the trioxide without loss by

<sup>1</sup> *Z. öffentl. Chem.*, 1906, 12, 263; *J. Chem. Soc. Abstr.*, 1906, 90, 707.



volatilisation. Care must be taken that the bottom of the platinum basin does not become more than faintly dull red hot. When the weight is constant, the contents of the basin are taken up with ammonia, which leaves only a few milligrams undissolved, consisting chiefly of silica, which is weighed and subtracted from the weight of the molybdic acid.  $\text{MoO}_3 \times 0.6667 = \text{Molybdenum}$ .

Of five specimens of the insoluble residue from the roasting process which were examined, four still contained very small quantities of molybdenum. A simple way of carrying out the qualitative test is to fuse with sodium carbonate, take up with hot water (if manganese is present, add alcohol), filter, faintly acidify, and add potassium ferrocyanide solution. If molybdenum is present, a characteristic red-brown coloration appears immediately. Pufahl has estimated these small quantities of molybdenum by von der Pfordten's method<sup>1</sup> by titrating with permanganate, after reducing with zinc and hydrochloric acid and diluting with water. (Larger quantities of the dissolved trioxide in sulphuric acid solution could not be quantitatively reduced to  $\text{Mo}_2\text{O}_3$  even by the use of magnesium (Glasmann).)<sup>2</sup> The solution must be strongly acid with hydrochloric acid; for less than 50 c.c. of molybdenum solution, about 75 c.c. of hydrochloric acid (sp. gr. 1.125), and not too little zinc (10 to 15 g.) are required. The reduction proceeds with great rapidity. The solution is then cooled quickly and considerably diluted. The permanganate required for the oxidation of the iron contained in the zinc must be determined in a blank experiment. The reaction is expressed by the following equation:—



A series of experiments with twenty solutions, containing from 20 to 50 mg. of molybdenum trioxide, gave very good results. Before titration, it is advisable to add a considerable quantity of concentrated manganous sulphate solution (200 g. of the crystallised salt in a litre) to the dilute solution, as is done in the titration with permanganate of ferrous solutions containing hydrochloric acid. In cases where the practical yield of molybdenum is to be determined, the fusion of the residue, etc., may be omitted.

(b) *Alternative Method*.—Five grams of a finely powdered good average sample are boiled down in an Erlenmeyer flask with 50 c.c. of concentrated nitric acid to about 10 c.c., the residue carefully taken up with ammonia, and warmed until all the molybdenum trioxide is dissolved. The solution is then washed into a litre flask, mixed with 50 c.c. of strong ammonium sulphide solution, and sulphuretted hydrogen passed in until the solution has acquired a deep brown-red

<sup>1</sup> Ber., 1882, 15, 1928; J. Chem. Soc. Abstr., 1883, 44, 122.

<sup>2</sup> Ber., 1905, 38, 604; J. Soc. Chem. Ind., 1905, 24, 251.

colour. The solution is now made up to the mark, well shaken, and an aliquot part, corresponding to about 0.5 g. of the substance, filtered through a dry filter. Molybdenum sulphide and sulphur are then precipitated by adding a slight excess of dilute sulphuric acid, filtered off, washed with hot water, dried, the filter paper incinerated in a Rose's crucible at a moderate temperature, the sulphide and a little sulphur added, heated, and finally ignited for a quarter of an hour in a current of hydrogen.  $\text{MoS}_2 \times 0.5996 = \text{Molybdenum}$ .

*Note.*—Molybdenite should be nearly pure, and contain as little as possible of other sulphides, especially sulphide of copper.

(c) *Technical Valuation of Molybdenite.*—For the technical valuation of molybdenite, H. Bornträger<sup>1</sup> digests about 1 g. of the finely ground molybdenite in an Erlenmeyer flask with 25 c.c. of concentrated nitric acid until the ore is completely decomposed (about two hours), and then drives off the nitric acid completely. The residue is extracted with ammonia, the solution filtered, the residue again treated with nitric acid and then with ammonia; the filtrates are mixed and evaporated to dryness with nitric acid. The residue, consisting of molybdic acid and ammonium nitrate, is treated with 50 per cent. alcohol to remove the ammonium nitrate, the molybdic acid collected on a weighed filter paper and weighed, after drying at 100°; or, it is dissolved in 50 c.c. of standard ammonia solution, and the excess of ammonia titrated back with sulphuric acid. By this means the practically available content of molybdenum is found.  $\text{MoO}_3 \times 0.6667 = \text{Molybdenum}$ .

## 2. Estimation of Molybdenum in Wulfenite.

(a) *Sulphuric Acid Method.*<sup>2</sup>—Half a gram of the substance, in the form of very fine powder, is heated for about twenty-four hours on a boiling water-bath, with 25 c.c. of sulphuric acid of sp. gr. 1.25, to which a few drops of nitric acid have been added. The solution is diluted with water, filtered, and the residue washed with water containing sulphuric acid. The filtrate from the lead sulphate is mixed with excess of ammonia, ammonium sulphide added, sulphuretted hydrogen passed in for a long time, and the analysis completed as in Method 1 (b).

In principle this method corresponds to that of C. Friedheim.<sup>3</sup>

(b) *Method of the Bleiberg Mines Union, Klagenfurth, for Wulfenite, Slags, and Residues containing Lead.*—Half a gram of the finely powdered substance is heated for about an hour with nitric acid, diluted with its own volume of water, in a covered porcelain basin on a sand-bath. A few cubic centimetres of sulphuric acid are then added, the mixture evaporated on the water-bath, and finally on the sand-bath,

<sup>1</sup> *Z. anal. Chem.*, 1898, 37, 438; *J. Soc. Chem. Ind.*, 1898, 17, 1184.

<sup>2</sup> Private communication from Dr C. Ahrens to Prof. Pufahl.

<sup>3</sup> Cf. *Ber.*, 1895, 28, 2061; 1896, 29, 2981; *J. Soc. Chem. Ind.*, 1896, 15, 220; 1897, 16, 263.

until sulphuric acid fumes are evolved, then diluted with water, the precipitate allowed to settle, filtered off, and washed with water containing sulphuric acid. The filtrate is diluted to 500 to 600 c.c., excess of ammonia and then 25 c.c. of yellow, freshly prepared ammonium sulphide added, filtered, heated, and dilute hydrochloric acid added, drop by drop, until the reaction is just acid. After boiling for a quarter of an hour, the very voluminous coarsely flocculent precipitate should settle quickly, and the liquid be quite colourless. A blue or brown colour shows the presence of molybdenum, which must be precipitated by sulphuretted hydrogen. The precipitate is filtered off, washed with hot water, dried, and separated from the filter paper, which is ignited by itself in a porcelain crucible. The precipitate is then added, the sulphur carefully burnt off, and the residue heated, at first gently, and finally more strongly, until the whole mass is converted into long yellowish white crystals of molybdic acid.

(c) *Fusion Method*.—This method is applicable both to wulfenite and molybdenite. One-half to one gram of the finely ground ore, dried at  $100^{\circ}$ , is fused in a porcelain crucible with six times the weight of sodium carbonate and sulphur. The fusion is extracted with water, the solution filtered, acidified with hydrochloric acid, warmed for some time, the very bulky molybdenum sulphide precipitate containing sulphur filtered through a weighed filter paper, and dried till constant. A considerable portion of this precipitate is then strongly ignited in a Rose crucible in a current of hydrogen; the sulphide is thus converted into the black sulphide  $\text{MoS}_2$ , and is weighed as such.  $\text{MoS}_2 \times 0.5996 = \text{Molybdenum}$ .

### 3. Estimation of Molybdenum in Ferro-molybdenum and in Molybdenum steel.

*Cf.* the section on "Iron," p. 74.

### 4. Detection of small quantities of Molybdenum in Ores, etc.

A few centigrams of the fine powder are heated on a porcelain lid with a few drops of distilled sulphuric acid until it fumes strongly; molybdenum, if present, dissolves as oxide, producing a deep blue colour.

## ALUMINIUM

Commercial aluminium always contains some silicon, iron, and a little copper as impurities; the content of aluminium varies between 96 and 99 per cent.

Other impurities found are: Carbon, nitrogen, sodium, lead, and traces of antimony, phosphorus, and sulphur. A somewhat high content



of sodium, according to Moissan, between 0.1 and 0.4 per cent., is specially injurious if the aluminium is to be employed for making ships' plates, cooking utensils, drinking flasks, etc.; as much as 4 per cent. has been found in some cases (Meissonier).

## A. TECHNICAL ANALYSIS OF ALUMINIUM<sup>1</sup>

### 1. Usual Method of Analysis.

This is restricted to the estimation of the silicon, iron, copper, and sodium.

1. *Total Silicon*.—One to three grams of metallic turnings are treated in a roomy, covered platinum dish with five to six times the weight of chemically pure sodium hydroxide<sup>2</sup> (prepared from metallic sodium) dissolved in 25 to 75 c.c. of water. After the first violent reaction is over, the contents of the dish are gently warmed, the cover-glass (a platinum cover is better) washed, hydrochloric acid added in excess, the solution evaporated, the silica rendered insoluble in the usual way, the residue dissolved by warming with hydrochloric acid and water, the solution cooled, the silica filtered off, and ignited in a platinum crucible. After weighing, the result is checked by treating the contents of the crucible on the water-bath with a few cubic centimetres of hydrofluoric acid and one drop of sulphuric acid, the solution evaporated, the sulphuric acid carefully driven off, and the residue strongly ignited and weighed.

The difference between the two weighings is silica.  $\text{SiO}_2 \times 0.4693 = \text{Silicon}$ .

The copper in the filtrate from the silica may be precipitated as sulphide by passing in sulphuretted hydrogen, filtered off, dissolved in a little hot nitric acid, and the copper in the solution either titrated or determined colorimetrically (*cf.* pp. 173 and 179). The iron may be determined by titration with potassium permanganate in the filtrate from the copper sulphide, after boiling the solution for half an hour to remove the sulphuretted hydrogen, largely diluting the cooled solution, and adding several cubic centimetres of sulphuric acid, and about 5 to 10 g. of crystallised sodium sulphate.

For the determination of the silicon, O. Handy<sup>3</sup> dissolves the metallic turnings in a mixture of 100 c.c. of nitric acid<sup>4</sup> (sp. gr. 1.42), 300 c.c. of hydrochloric acid (sp. gr. 1.2) and 600 c.c. of 25 per cent. sulphuric acid; by the use of this acid mixture, none of the silicon is

<sup>1</sup> *Cf.* R. Seligman and F. J. Willott, *J. Inst. Metals*, 1910, 3, 138.

<sup>2</sup> Regelsberger, "Valuation of Aluminium and its Alloys," *Z. angew. Chem.*, 1891, 4, 442, 473; *J. Chem. Soc. Abstr.*, 1893, 64, 48.

<sup>3</sup> *J. Amer. Chem. Soc.*, 1896, 18, 766; *J. Chem. Soc. Abstr.*, 1897, 72, 191.

<sup>4</sup> *Cf.* Moissan, *Comptes rend.*, 1905, 121, 851; Sibbers, *Pharm. Zeit.*, 1907, 42, 622.

evolved as hydride. One gram of the metal is treated in a covered porcelain dish with 20 to 30 c.c. of the acid mixture, gently warmed until the metal is completely attacked, the solution evaporated, and the residue heated until fumes of sulphuric acid are evolved. The cooled residue is next warmed for some time with 100 c.c. of 25 per cent. sulphuric acid; 100 c.c. of boiling water are then added, the sulphate completely dissolved by boiling, the mixture of silica and silicon filtered off, the filter paper ignited in a platinum crucible, the residue fused with 1 g. of sodium carbonate, the silica separated from the fusion in the usual way (decomposition with hydrochloric or sulphuric acid, evaporating, etc.), weighed, and its purity determined by evaporating with hydrofluoric acid, etc., as above. The silica thus found represents the total silicon content.

2. *Graphitic (crystalline) Silicon*.—The mixture of silica and silicon obtained as above from a separate weighing is treated in a platinum crucible with several cubic centimetres of hydrofluoric acid and one drop of sulphuric acid, the solution evaporated, the sulphuric acid driven off, the brown residue (silicon) strongly ignited and weighed, after half an hour. The difference between the weight of silicon thus found and the weight of total silicon estimated previously gives the content of combined silicon.<sup>1</sup>

Since sodium or potassium hydroxide invariably contains silica, it should not be used for the determination of silicon in aluminium.

3. *Iron*.—According to O. Handy, 1 g. of the metal is dissolved in 20 to 30 c.c. of the acid mixture described above (1), the solution evaporated until sulphuric acid fumes are copiously evolved, the residue taken up by warming with dilute sulphuric acid, the ferric sulphate in the solution reduced by 1 g. of pure zinc, and the cooled, diluted solution titrated with potassium permanganate.

Regelsberger<sup>2</sup> dissolves 3 g. of turnings in a 500 c.c. flask in a sufficient quantity of 30 to 50 per cent. potassium hydroxide, finally warming, adds 200 c.c. of dilute sulphuric acid (sp. gr. 1.16) with shaking, boils until the solution clears, cools, and titrates with permanganate.

4. *Copper*.—One gram of turnings are treated in a platinum dish with 5 g. of sodium hydroxide and 25 c.c. of water, the solution diluted, the residue consisting of copper and iron filtered off and well washed, dissolved in a few cubic centimetres of hot, dilute nitric acid, the iron precipitated by adding excess of ammonia, the ferric hydroxide filtered off, and the copper in the filtrate determined colorimetrically (*cf.* p. 179). In the case of a large content of copper (aluminium is frequently alloyed with copper), it is determined by electrolysis.

O. Handy dissolves 1 g. of turnings by warming with 20 c.c. of

<sup>1</sup> *Cf.* Hunt, Clapp, and Handy, *Chem. News*, 1902, 65, 223, 235.

<sup>2</sup> *Loc. cit.*

33 per cent. sodium carbonate solution (five volumes of a cold, saturated solution of sodium carbonate diluted with one volume of water), and filters the copper and iron off, etc., as above.

5. *Sodium*.—Moissan<sup>1</sup> dissolves 5 g. of metal in hot, dilute nitric acid (1 : 2), evaporates the solution in a platinum dish, dries the residue, and heats it for a considerable time to a temperature somewhat lower than the fusion temperature of the sodium nitrate. The aluminium nitrate is completely decomposed.<sup>2</sup> The sodium nitrate is extracted from the ignited residue by means of hot water, the solution evaporated in a porcelain dish, the evaporation twice repeated with hydrochloric acid, the thoroughly dried residue dissolved in water, and the chlorine in the sodium chloride solution either precipitated or titrated with silver nitrate.

Since some aluminium may easily go into solution as sodium aluminate, it is advisable to evaporate the sodium nitrate solution with a slight excess of sulphuric acid, to then digest the solution with some ammonium carbonate solution, filter, and by evaporating the filtrate and igniting the residue in a platinum crucible, to determine the sodium as sulphate in the usual way. If it is desired to determine the content of sodium by the usual analytical methods, *e.g.*, dissolving the aluminium in dilute hydrochloric acid, passing in sulphuretted hydrogen, filtering, boiling off the sulphuretted hydrogen, oxidising, saturating the solution with ammonia, boiling, evaporating the filtrate with several drops of sulphuric acid, etc., only absolutely pure water and ammonia must naturally be used, and the operation carried out so far as possible in platinum vessels.

## 2. More Complete Analysis.

This includes the determination of aluminium, carbon, lead, phosphorus, sulphur, arsenic, and nitrogen.

1. *Aluminium*.—One to five grams of an average sample are dissolved in a large flask in very dilute hydrochloric acid (1 : 5), finally warming, sulphuretted hydrogen passed in, after cooling, the solution filtered into a measuring flask, and the filter paper and precipitate washed with water containing dilute hydrochloric acid and sulphuretted hydrogen water. After filling up to the mark, a volume of the solution corresponding to 0.2 g. of the sample is withdrawn with a pipette, the solution run into a large platinum dish, the sulphuretted hydrogen driven off by heating, and the iron in the solution oxidised with a few drops of bromine water. The solution is then diluted to 200 to 300 c.c., excess of ammonia added, the dish covered, the contents boiled until the ammonia is completely expelled, the precipitate filtered off, washed

<sup>1</sup> *Comptes rend.*, 1895, **121**, 851 ; *J. Soc. Chem. Ind.*, 1896, **15**, 136.

<sup>2</sup> Deville, *Ann. Chim. Phys.*, 1853, **3**, 38.



with boiling water until the runnings cease to give a chloride reaction, the impure aluminium hydroxide dried, ignited over the blowpipe, and weighed. The iron is determined in a separate analysis, and is deducted as ferric oxide (*cf.* p. 347).  $\text{Al}_2\text{O}_3 \times 0.5303 = \text{Aluminium}$ .

In general practice it is unusual to determine the amount of aluminium present, the impurities only being determined and the aluminium obtained by difference.

2. *Carbon*.—Regelsberger<sup>1</sup> recommends direct combustion in the wet way by means of chromic and sulphuric acids; Corleis's apparatus (*cf.* Iron, pp. 49 *et seq.*) is specially suitable for the estimation.

H. Moissan treats 10 g. of aluminium with concentrated potassium hydroxide solution, thoroughly washes the residue containing the carbon on an asbestos filter, dries in a porcelain boat, oxidises the carbon in a current of oxygen, and collects the carbon dioxide in potash bulbs. According to Moissan, aluminium only contains combined carbon; he found from 0.08 to 0.104 per cent. in various samples.

Moissan, Gouthière, and others also recommend the separation of the carbon by means of mercuric chloride, according to Boussingault's method.

3. *Lead*.—If the aluminium is dissolved, etc., by Handy's method (p. 346), the lead will be found as sulphate, together with the mixture of silica and silicon. The lead sulphate is extracted with a hot solution of ammonium acetate, and precipitated from the acetate solution either by sulphuretted hydrogen or by potassium chromate.

4. *Phosphorus, Sulphur, and Arsenic* are determined, according to M. Jean,<sup>2</sup> by dissolving 10 g. of the metal in very dilute hydrochloric acid and passing the impure hydrogen evolved into bromine water (*cf.* Determination of Sulphur in Iron, p. 80). The solution in the receiver is divided into two portions; the sulphur is estimated as barium sulphate, the arsenic by precipitation with sulphuretted hydrogen, etc., and in the filtrate from the arsenic sulphide the phosphoric acid by means of molybdic acid solution. H. Gouthière<sup>3</sup> determines the sulphur by igniting several grams of the finely divided metal in a current of pure hydrogen, passing the hydrogen through an ammoniacal solution of silver, filtering off the precipitated silver sulphide, washing, drying, igniting, and weighing as metallic silver.  $\text{Ag} \times 0.1486 = \text{Sulphur}$ .

5. *Nitrogen*.—Moissan dissolves a somewhat large sample in pure 10 per cent. potassium hydroxide, distils off the ammonia formed into dilute hydrochloric acid, and estimates it colorimetrically with Nessler's solution.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Campredon, *Guide pratique du Chimiste Metallurgiste*, p. 271.

<sup>3</sup> *Ann. de Chemie analyt.*, 1 [14], 265; *J. Soc. Chem. Ind.*, 1896, 15, 830.

## B. ALUMINIUM ALLOYS

Alloys of aluminium with nearly all the heavy metals are known. The iron aluminium alloys (ferro-aluminium) and the copper aluminium alloys, or aluminium bronzes, are of special importance.

**1. Aluminium with Copper.**—Three to eight per cent. of copper is added to aluminium to increase the strength; many useful articles are made of such alloys. Alloys rich in copper (with 20 to 40 per cent.), prepared in the electric furnace at aluminium works, do not come into commerce, but are used for the manufacture of aluminium bronzes (cf. *infra*).

*Determination of Copper* (cf. p. 346).—The washed residue left after treating the metallic turnings with sodium hydroxide or with 33 per cent. sodium carbonate solution is dissolved in hot, dilute nitric acid, and the copper deposited from the solution electrolytically. Alloys containing more than 8 per cent. of copper are dissolved in dilute nitric acid, the solution evaporated with excess of sulphuric acid, the residue taken up with water, the silica filtered off, and the filtrate electrolysed.

For alloys with more than 50 per cent. of aluminium, the following method is convenient (Bannister):—The alloy is treated with dilute hydrochloric acid, when a vigorous action sets in and all the aluminium goes into solution, whilst the copper is separated in a spongy form. If the copper is filtered off as soon as the evolution of hydrogen ceases, none will be left in the solution, but should any remain, it is precipitated by means of sulphuretted hydrogen. The whole of the copper is then dissolved in nitric acid and electrolysed in the usual manner.

**2. Aluminium with Nickel and Copper.**—Aluminium is alloyed with up to 3 per cent. of nickel, and at the same time some copper is added.

*Determination of Nickel and Copper.*—One to five grams of turnings are decomposed as described under 1, the copper deposited electrolytically from the nitrate solution, the solution from the copper evaporated with excess of sulphuric acid until fumes of sulphuric acid begin to be evolved, the cooled residue dissolved in 20 to 50 c.c. of water, a large excess of ammonia added, and the nickel separated electrolytically.

**3. Aluminium with Manganese.**—Five grams of turnings are treated in a large flask with 50 c.c. of water, to which small quantities of hydrochloric acid are added, until the metal is completely dissolved. One c.c. of nitric acid (sp. gr. 1.4) and 5 c.c. of sulphuric acid are then added and the solution boiled down, the syrupy residue taken up with water, nearly neutralised with sodium hydroxide, poured into a litre flask, a small excess of moist, precipitated zinc oxide added, the contents of the flask made up to the mark, shaken for some time, and

the manganese, in a portion of the liquid after filtration through a dry filter paper, titrated according to Volhard's method (*cf.* Iron, pp. 34 *et seq.*). If the manganese content is very low, the hydrochloric acid solution from 5 to 10 g. of metal is evaporated, the residue repeatedly boiled with strong nitric acid, and, after a fresh addition of nitric acid, the manganese separated as hydrated peroxide by means of potassium chlorate, according to Hampe's method; the precipitated oxide is washed, dissolved in an acid solution of ferrous sulphate of known strength, and the excess of ferrous sulphate titrated back (*cf.* Iron, pp. 161 *et seq.*).

**4. Aluminium with Tungsten.**—The content of tungsten generally amounts to less than 2 per cent.

Five grams of the alloy are dissolved in dilute hydrochloric acid (1:2), 20 c.c. of strong nitric acid added, the solution boiled down, the residue taken up with 50 c.c. of ordinary hydrochloric acid and 100 c.c. of water, boiled for from one to two hours, the mixture of silicon, silica, and tungstic acid filtered off, washed, the filter paper and contents ignited, fused with sodium carbonate, and the melt repeatedly evaporated to dryness with hydrochloric acid. After finally heating the residue to about 150°, it is allowed to cool, heated on a boiling water-bath with 20 c.c. of hydrochloric acid, 50 c.c. of water added, the mixture of silica and tungstic acid filtered off, washed, the filter paper and contents ignited in a platinum crucible, the silica removed by evaporating with several cubic centimetres of hydrofluoric acid and one drop of sulphuric acid, the sulphuric acid driven off, and the pure tungstic acid ignited and weighed.  $\text{WO}_3 \times 0.7931 = \text{Tungsten}$ .

**5. Aluminium with Chromium.**—Five grams of the alloy are dissolved in hydrochloric acid, the solution boiled down with an excess of sulphuric acid (18 c.c.) until the hydrochloric acid is completely driven off, diluted with 100 c.c. of water, the greater part of the free acid neutralised with sodium hydroxide, 5 to 10 c.c. of potassium permanganate solution<sup>1</sup> (1 c.c. = 5 mg. Fe) added, the solution boiled for five minutes, filtered through a dense filter paper, and the precipitate washed with boiling water. All the chromium in the alloy is contained in the yellow solution as chromic acid. The cooled solution is acidified with dilute sulphuric acid, a weighed quantity (an excess) of ferrous ammonium sulphate added, the solution stirred, and the excess of ferrous sulphate in the colourless solution titrated back with a solution of permanganate (*cf.* p. 323); 335.1 parts of iron correspond to 104.2 parts of chromium; 100 parts of ferrous ammonium sulphate contain 14.247 parts of iron.

**6. Iron-Aluminium Alloys** (Ferro-aluminium and Ferro-silicon-aluminium).

<sup>1</sup> *Cf.* H. Peterson, *Chem. News*, 1884, 50, 210; *J. Soc. Chem. Ind.*, 1885, 4, 244.



These alloys contain up to 15 per cent. of aluminium (generally 10 per cent.) and up to 15 per cent. of silicon; they are used in large quantities as additions to cast iron and for the deoxidation of steel. The content of aluminium is best determined either by J. Rothe's ether-separation method (*cf.* Iron, pp. 9-11), or by Baudisch's "Cupferron" method (p. 172).

**7. Copper-Aluminium Alloys** (Aluminium bronzes).—Of these alloys, those containing approximately 5 and 10 per cent. of aluminium respectively possess valuable properties and are of wide application.

For their analysis, 1 g. of turnings is dissolved in a covered porcelain dish by warming with 10 c.c. of nitric acid (sp. gr. 1.2), the solution evaporated with 10 c.c. of 50 per cent. sulphuric acid, and the residue heated until sulphuric acid fumes are evolved. The cooled residue is warmed for some time with 30 c.c. of water, the solution cooled, and the silica filtered off. Any lead present is found as sulphate with the silica; it is dissolved out with a hot solution of ammonium acetate, and the lead precipitated with sulphuretted hydrogen and estimated as sulphate (*cf.* p. 222). The washed silica is dried, ignited, and weighed.  $\text{SiO}_2 \times 0.4693 = \text{Silicon}$ .

The copper is deposited electrolytically in the filtrate from the silica, after the addition of a small quantity of nitric acid (0.5 c.c.); the solution from the copper is largely diluted, saturated with ammonia, boiled, and the aluminium separated as hydroxide containing iron, and estimated as described under 2, 1. The ignited mixed oxides are fused up with six times their weight of acid potassium sulphate, the cooled fusion dissolved in hot, dilute sulphuric acid, reduced with zinc, the iron titrated with permanganate, calculated to ferric oxide, and subtracted from the impure alumina.

**8. Magnesium-Aluminium Alloys.**—Such alloys, known as "Magnalium," have recently been recommended as specially strong and of low specific gravity. (The specific gravity of cast aluminium is 2.64, that of magnesium 1.75.)

For their analysis, 1 g. of the alloy is dissolved in the acid mixture recommended by O. Handy (p. 346), the silicon determined, sulphuretted hydrogen passed into the filtrate from the silica, any precipitated copper sulphide filtered off, and the filtrate diluted to 300 c.c.; 100 c.c. are boiled to expel the sulphuretted hydrogen, the solution cooled, and the iron titrated with permanganate. Two hundred c.c. are similarly freed from sulphuretted hydrogen, a few cubic centimetres of bromine water added to oxidise the ferrous sulphate, the solution cooled, neutralised with sodium carbonate, 30 c.c. of concentrated ammonium acetate solution added, largely diluted, the aluminium and iron precipitated by boiling, and the magnesium in the evaporated filtrate separated as usual with phosphoric acid and ammonia. The weight of ferric

oxide found by the estimation of the iron is deducted from the weight of ignited alumina containing ferric oxide. The magnesium is weighed as magnesium pyrophosphate.  $\text{Mg}_2\text{P}_2\text{O}_7 \times 0.2185 = \text{Magnesium}$ .

#### 9. Solders for Aluminium and Aluminium Bronzes, etc.—

Numerous alloys are used as “solders,” *e.g.*, an alloy of silver and aluminium which melts easier than aluminium; or an alloy of ten parts of aluminium with ten parts of 10 per cent. phosphor-tin, eighty parts of zinc, and two hundred parts of tin. In addition, alloys of tin and aluminium; of tin, zinc, aluminium, copper, and silver; of zinc, aluminium, copper, etc., are employed. Recently, cadmium has been frequently introduced into aluminium solders. The procedure for the analysis is necessarily dependent on the result of the qualitative analysis.

In the analysis of scrap aluminium, constituents of the solder are usually found, and must be taken into account.

For commercial scrap aluminium, the following procedure is recommended by Kluss; the determination of the silicon is carried out as described under 1, 1:—One to two grams of the turnings are dissolved in dilute hydrochloric acid, small quantities of potassium chlorate being finally added, the solution evaporated to separate the silica, the residue taken up with hydrochloric acid and water, the silica and silicon filtered off, and sulphuretted hydrogen passed into the filtrate. The precipitated sulphides are collected on a small filter paper, washed, washed off the paper into a beaker, the precipitate adhering to the paper dissolved off in hot, dilute nitric acid, the sulphides boiled with nitric acid, the solution diluted with hot water and again boiled. After settling, the impure tin oxide is filtered off through the filter paper previously used, ignited, and weighed, then fused up with sodium carbonate and sulphur (or dehydrated sodium thiosulphate), the product extracted with hot water, any copper sulphide and lead sulphide remaining behind dissolved in nitric acid, and the lead separated and weighed as sulphate, which is deducted from the original weight of impure tin oxide. The copper is deposited electrolytically in a platinum crucible from the acid filtrate from the lead sulphate. The solution from the copper may still contain cadmium, which is precipitated with sulphuretted hydrogen, and finally weighed as cadmium sulphate (*cf.* p. 303).

The filtrate from the first precipitation with sulphuretted hydrogen is boiled to expel the sulphuretted hydrogen, after cooling, a few drops of Congo red added, and ammonia added, drop by drop, until the blue coloration is just turned red. Two grams of ammonium sulphate are then added, sulphuretted hydrogen passed in for one hour, and the precipitated zinc sulphide estimated as such (*cf.* p. 288). The sulphuretted hydrogen is boiled off from the filtrate from the zinc, a few drops of bromine water being finally added, the solution cooled, diluted to

500 c.c., and one portion used for the combined determination of aluminium and iron; a second portion is evaporated with hydrochloric acid, the residue taken up with hydrochloric acid and water, potassium iodide added, and the free iodine titrated with standard sodium thio-sulphate, thus determining the content of iron.

**10. Aluminium Brass.**—This is analysed by the method described on pp. 216 *et. seq.*

## THORIUM

Owing to the extended use of thorium nitrate in the manufacture of incandescent gas mantles, the raw materials from which it is prepared, especially monazite sand, have become important articles of commerce, and their valuation has frequently to be carried out.

An average sample of from 1 to 5 g. suffices for the analysis; in the laboratories of factories where thorium nitrate is manufactured, it is usual, before buying, to make an experiment on a manufacturing scale with 10 to 20 kg. of raw material, from which the yield of thorium nitrate is estimated.

**Analysis of Thorite** (also known as Orangite, Monazite, etc.).—This is best effected by the method worked out by E. Hintz and H. Weber.<sup>1</sup> One gram of the very finely powdered substance is decomposed by warming with 10 to 15 c.c. of fuming hydrochloric acid, and the solution evaporated to dryness to separate silica. The residue is moistened with 2 c.c. of concentrated hydrochloric acid, digested, water added, and the silica filtered off. To separate copper and lead, sulphuretted hydrogen is passed in, the solution filtered, the sulphuretted hydrogen removed by boiling, the liquid diluted with 200 c.c. of water, heated, and precipitated with a solution of 1 g. of oxalic acid. After standing for two days, the precipitate (thorous oxalate, cerous oxalate, etc.) is filtered off, thoroughly washed, and treated for several hours in a boiling water-bath with 60 c.c. of a cold, saturated solution of ammonium oxalate. The solution is then diluted with 300 c.c. of water, filtered, after standing for two days, and the residue washed with water containing a trace of ammonium oxalate. The extraction of the oxalates is repeated with quantities of 20 c.c. of ammonium oxalate solution, saturated in the cold, as long as weighable precipitates of thorous oxalate are obtained by acidifying the filtrate (100 c.c. each time) with 1.7 c.c. of hydrochloric acid. The filtrate is mixed with 5 c.c. of strong hydrochloric acid, heated, and after standing for two days the separated thorous oxalate is filtered off, washed with water faintly acidulated with hydrochloric acid, dried, ignited to thorium oxide ( $\text{ThO}_2$ ), and weighed. The precipitate is

<sup>1</sup> *Z. anal. Chem.*, 1897, 36, 27; *J. Soc. Chem. Ind.*, 1897, 16, 357.



always contaminated with traces of the oxides derived from cerite and yttria. For their separation, the ignited oxide is fused with potassium hydrogen sulphate, the melt dissolved in water containing hydrochloric acid, the solution diluted, precipitated with ammonia, the precipitate filtered off, washed, dissolved in hydrochloric acid, and the solution evaporated. The residue is taken up with water and two to three drops of ordinary hydrochloric acid, diluted to 300 c.c., 3 to 4 g. of sodium thiosulphate added, and the solution boiled for a few minutes. After cooling, the precipitated thoria is filtered off and washed. The filtrate is precipitated with ammonia, the precipitate washed thoroughly on the filter, dissolved in hydrochloric acid, the solution evaporated to dryness, the residue taken up with a little water, boiled, hot, concentrated ammonium oxalate solution added, and the boiling continued for a few minutes; the solution is then considerably diluted and allowed to stand for a long time in the cold. The separated oxalates of the cerite oxides and of yttria are then filtered, ignited, and the weight of the oxides subtracted from that of the oxide from the impure thoria.

*Monazite Sand* can also be analysed by this method, but on account of its small content of thoria (rarely above 6 to 8 per cent.), a larger quantity, from 5 to 20 g., should be taken for analysis. The very fine powder is usually decomposed by prolonged heating to about 200° with an equal weight of concentrated sulphuric acid, and the cold solution transferred, in small portions at a time, to water cooled with ice. The extraction with boiling ammonium oxalate solution must be repeated many times, since relatively little thorous oxalate requires to be extracted from a large quantity of oxalates of the ceria oxides and of yttria.

**Determination of Thorium in Monazite Sand.**—E. Benz<sup>1</sup> recommends the following shortened method:—Half a gram of “bagged” monazite sand is intimately admixed in a platinum crucible with 0.5 g. of sodium fluoride, and gradually heated with 10 g. of potassium pyrosulphate until the fusion is tranquil, the lid being kept on the crucible. The heating is best carried out by fixing the platinum crucible, by means of an asbestos ring, into a large porcelain crucible. When the evolution of gas has ceased, the contents of the crucible are further heated to a dull red heat for about fifteen minutes over a free flame, after which the fused mass is lixiviated on the water-bath with water and hydrochloric acid. After settling, the solution is filtered off, the residue again boiled with concentrated hydrochloric acid, the solution diluted, and again filtered. The greater part of the free acid in the filtrate (about 300 c.c.) is neutralised with ammonia (the neutralisation must not be carried too far, since if a

<sup>1</sup> *Z. angew. Chem.*, 1902, 15, 297; *J. Soc. Chem. Ind.*, 1902, 21, 563.

precipitate is formed, it is very difficult to redissolve), and 3 to 5 g. of ammonium oxalate are added to the boiling solution, the solution being vigorously stirred with a glass rod; the oxalates settle immediately as a coarse granular precipitate. The solution is always tested to see if a further addition of ammonium oxalate produces any precipitate. After standing overnight, the oxalates are filtered off, washed with hot water, and washed off the filter paper into a porcelain dish with the smallest possible quantity of water. The filter paper is repeatedly washed with hot, concentrated nitric acid and water, and then the contents of the dish evaporated nearly to dryness on the water-bath. Several cubic centimetres of pure nitric acid are first added to the residue, then 10 c.c. of fuming nitric acid, the dish covered with a clock-glass, and again placed on the water-bath. When the evolution of gas, due to the decomposition of the oxalates, has quite ceased, the clock-glass and the sides of the dish are washed down with water, and the solution evaporated to dryness. In order to completely drive off all the free nitric acid, the evaporation is repeated with 20 c.c. of water. The residue is then taken up with 20 c.c. of water, the solution freed from impurities by filtering, several cubic centimetres of a saturated solution of ammonium nitrate added to the filtrate, the solution diluted to 100 c.c., heated to 60° to 80°, and the thorium precipitated as peroxide by the addition of about 10 c.c. of distilled 2 to 3 per cent. hydrogen peroxide. The precipitate is filtered off, washed, partially dried, the filter paper and precipitate placed in a platinum crucible, the crucible first gently heated with the lid on, and the temperature then gradually increased, the lid removed, and the crucible finally strongly ignited and the contents weighed as thorium oxide.  $\text{ThO}_2 \times 0.8790 = \text{Thorium}$ .

Three analyses, carried out on 0.5 g. of substance, gave a mean percentage of 4.60 of thorium oxide in a monazite sand; these results agreed extremely well with the figures obtained (4.59 and 4.63 per cent.), using an extended method of analysis.<sup>1</sup>

**Thorium Nitrate.**—The good commercial product consists of a dry crumbly white salt-like material which, on strong ignition, leaves a 47 to 49 per cent. residue of snow-white and very bulky thorium oxide. The product is never chemically pure; it always contains recognisable quantities of other rare earths, and usually also traces of iron, calcium, and magnesium oxides, alkalis, and sulphuric acid.

<sup>1</sup> E. Benz, *loc. cit.*

## TANTALUM

This metal is now of considerable importance, owing to its extensive use in metallic filament electric lamps.

The chief minerals are<sup>1</sup>:—*Tantalite*, a tantalate of iron and manganese,  $\text{FeMnTa}_2\text{O}_6$ , which often contains small quantities of calcium, cupric oxide, etc.; and *Yttrotantalite*,  $5\text{YO} \cdot \text{Ta}_2\text{O}_5$ . In addition, tantalum occurs with columbium in several minerals, of which *Columbite* is the most important, which often contains tantalum (in some cases up to 50 per cent.  $\text{Ta}_2\text{O}_5$ ); *Hatchettolite* is chiefly a tantalocolumbate of uranium; *Fergusonite* consists mainly of columbate and tantalate of yttrium.

METHODS OF ANALYSIS<sup>2</sup>

## 1. Rammelsberg's Method.

Usually the mineral, in the finest possible powder, is decomposed by fusing with eight to ten times its weight of potassium hydrogen sulphate, and the fused mass extracted with boiling water, which dissolves the sulphates of iron, manganese, and possibly copper; the residue consists of tantalum pentoxide,  $\text{Ta}_2\text{O}_5$ , and columbic oxide,  $\text{Cb}_2\text{O}_5$ , frequently contaminated by stannic oxide, tungsten trioxide, and silica. In the latter case the tin and tungsten are extracted by digestion with ammonium sulphide, the residue filtered off, washed with water containing ammonium sulphide, any ferrous sulphide produced removed by hot hydrochloric acid, and the silica finally volatilised with hydrofluoric and sulphuric acids. The "earth acids" purified in this way are dissolved, by warming, in strong hydrofluoric acid, potassium hydrogen fluoride added (according to A. Tighe,<sup>3</sup> preferably double the supposed weight of the metals), when the tantalum separates from the sufficiently concentrated solution in the form of difficultly soluble (1:200 in water) crystalline needles of tantalum potassium fluoride, whilst the corresponding columbium compound remains dissolved.

This separation by fractional crystallisation gives tolerably accurate results. By heating the double fluoride to  $400^\circ$  with an equal weight of concentrated sulphuric acid, extracting the residue with boiling water, and strongly igniting it, finally, after adding ammonium carbonate, pure tantalic acid is obtained.  $\text{Ta}_2\text{O}_5 \times 0.819 = \text{Tantalum}$ .

The actual decomposition of tantalite can be effected by fusing the powdered ore with potassium carbonate at a high temperature or with

<sup>1</sup> Cf. *Mineral Industry*, 1909, 17, 799.

<sup>2</sup> Cf. *Pogg. Ann.*, 1872, 146, 56.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1906, 25, 681.



potassium hydroxide, when readily soluble potassium tantalate and columbate are formed (cf. *infra*, Methods of Giles and of Simpson).

## 2. Kunheim & Co.'s Method.<sup>1</sup>

Twenty grams of the material in the finest powder are heated for about an hour with 200 g. of potassium hydrogen sulphate in a platinum basin, at first over a low flame, and finally fused over the blowpipe. The fused mass is extracted with a considerable volume of boiling water, the residue collected on a filter, and after washing, treated with hydrofluoric acid (20 per cent.). If it does not dissolve completely, the fusion with bisulphate, etc., must be repeated. The hydrofluoric acid solution is warmed to about 70°, and a cold, saturated solution of potassium hydrogen fluoride added as long as a precipitate of tantalum potassium fluoride results; this is easily observed, as the precipitate settles rapidly. While the solution cools, it must be carefully examined for fine needles (of columbium potassium fluoride) on the edge of the basin, which, if formed, must be filtered off at once; otherwise, the basin is allowed to stand for two hours. Filtration is preferably carried out by suction, in a vulcanite funnel provided with a sieve plate. The residue is then washed with a small quantity of cold water and allowed to stand for a time.

The filtrate is evaporated to half its volume; if a further precipitation occurs, it is assumed to be chiefly potassium tantalum fluoride, and, after filtering and washing, is added to the bulk of the precipitate.

The tantalum precipitates, whilst still in a moist state, or if much tantalum is present, previously dried, are stirred up with concentrated sulphuric acid in a platinum basin, and the sulphuric acid completely evaporated off. The residue is extracted with boiling water, filtered, the residual crude tantalic acid again dissolved in hydrofluoric acid, and the precipitation with potassium hydrogen fluoride repeated.

The purified potassium tantalum fluoride,  $K_2TaF_7$ , is decomposed by concentrated sulphuric acid, the residue extracted with boiling water, filtered off, and the dried residue strongly ignited, and the ignition repeated after addition of ammonium carbonate to ensure the removal of the residual trace of sulphuric acid. The residue is then weighed as tantalum pentoxide,  $Ta_2O_5$ .

The determination of columbium is effected by precipitating the filtrates from the potassium tantalum fluoride with ammonia. The precipitate is filtered off, washed, evaporated with sulphuric acid, the residue extracted with boiling water, and the columbic acid weighed after strong ignition, finally with ammonium carbonate.  $Cb_2O_5 \times 0.7015$  = Columbium.

<sup>1</sup> Private communication to Prof. Pufahl.

### 3. W. B. Giles' Method.<sup>1</sup>

The finely powdered mineral, intimately mixed with two and a half to three times its weight of potassium carbonate, is fused for an hour in a steel crucible in a Griffin's radial gas furnace. The fused mass is easily separated from the crucible; any tin present clings to the sides. The melt is extracted with hot water, when potassium tantalate and columbate are easily dissolved; iron and manganese remain as black oxides in the form of a heavy crystalline sand. (In presence of much tin, carbon or argol is added.) The volume of the solution is about 1 litre when 25 g. of the substance have been used. Four to five c.c. of potassium sulphide solution are added, and the black liquid poured into a mixture of 80 to 100 c.c. of concentrated hydrochloric acid (rather more than equivalent to the potassium carbonate), diluted with about 900 c.c. of water, and the whole heated to separate the acids. The precipitate is washed by decantation, dissolved in hydrofluoric acid, and separated (as above) by fractional crystallisation.

### 4. E. S. Simpson's Method.<sup>2</sup>

The ore is fused in a nickel or silver crucible with a large excess, about twelve times its weight, of potassium hydroxide, the melt extracted with water, acidified with hydrochloric acid, the acid hydroxides precipitated by boiling (as in Giles' method), dissolved in hydrofluoric acid, and the tantalum separated as the double potassium fluoride from columbium. Columbium is precipitated as hydroxide in the filtrate from the potassium tantalum fluoride and weighed as  $\text{Cb}_2\text{O}_5$ . In a second portion (the solution first obtained from the melt is divided) the total weight of the pentoxides,  $\text{Ta}_2\text{O}_5 + \text{Cb}_2\text{O}_5$ , is determined, and the quantity of tantalic acid obtained by difference. Tin, iron, and manganese are determined in the hydrochloric acid filtrate from the mixture of the acid hydroxides.

## METALLIC SALTS

### IRON SALTS

**Ferrous Sulphate**,  $\text{FeSO}_4 + 7\text{H}_2\text{O}$  (Green Vitriol).—The pure salt forms light bluish green monoclinic prisms, which quickly effloresce in dry air and become opaque; in moist air the crystals oxidise and gradually become transformed into yellowish brown basic ferric sulphate.

Ferrous sulphate is insoluble in alcohol, ether, and concentrated sulphuric acid; the latter reagent separates  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  from concentrated aqueous solutions. It is soluble to a considerable extent in water; one part of the sulphate is dissolved by one and a half parts of cold

<sup>1</sup> *Chem. News*, 1909, 99, 1.

<sup>2</sup> *Ibid.*, 1908, 99, 243.

water and one-third part of water at  $100^{\circ}$ . According to determinations by Gerlach, pure aqueous solutions at  $15^{\circ}$  contain the following amounts of  $\text{FeSO}_4 + 7\text{H}_2\text{O}$ , expressed in percentages by weight:—

Per cent. $\text{FeSO}_4 + 7\text{H}_2\text{O}$ .	Spec. grav.	Per cent. $\text{FeSO}_4 + 7\text{H}_2\text{O}$ .	Spec. grav.
1	1.005	15	1.082
2	1.011	20	1.112
3	1.016	25	1.143
4	1.021	30	1.174
5	1.027	35	1.206
10	1.054	40	1.239

The content of iron is best determined by titrating a dilute solution, acidified with sulphuric acid, with potassium permanganate (*cf.* Vol. I., p. 99).

Intentional adulteration of the salt is not met with. Ferric oxide is recognised by adding potassium ferrocyanide or potassium thiocyanate to the dilute hydrochloric acid solution. Copper is detected by oxidising the hydrochloric acid solution by boiling with nitric acid, precipitating with ammonia, and filtering off the ferric hydroxide; a blue coloration in the filtrate indicates copper. Small quantities are more definitely recognised by rendering the ammoniacal filtrate just acid with hydrochloric acid, and adding several drops of potassium ferrocyanide, whereby a reddish brown precipitate or cloudiness of copper ferrocyanide is produced. If the sulphate contains copper, 1 to 2 g. are dissolved in hydrochloric acid, the solution diluted, sulphuretted hydrogen passed in, warmed, the copper sulphide filtered off, the ferrous salt in the filtrate oxidised, etc., and the iron precipitated by boiling with sodium acetate. Zinc is detected in the filtrate by the white precipitate of zinc sulphide produced on passing sulphuretted hydrogen. If a black precipitate of nickel sulphide is produced, it must be specially tested for admixture of zinc sulphide. Manganese very frequently occurs in ferrous sulphate, and is recognised by the brown precipitate produced when the filtrate from the basic acetate of iron is heated with sodium hydroxide and bromine water. In order to detect aluminium (the presence of which, for many uses of ferrous sulphate, is specially detrimental), the iron precipitate is treated in a platinum dish with hot, pure sodium hydroxide solution (prepared from metallic sodium), the contents of the dish diluted, the precipitate filtered off, the filtrate neutralised with acetic acid and then boiled, whereby any aluminium present is precipitated.

**Ferric Sulphate**,  $\text{Fe}_2(\text{SO}_4)_3 + aq$ .—This salt is prepared by the oxidation of a hot, concentrated sulphuric acid solution of ferrous sulphate by means of nitric acid. It usually comes into commerce dissolved as a brown liquid of sp. gr. 1.45 to 1.53, which is used in



dyeing; it is also less frequently met with in the solid state as a whitish salt-like material.

For the estimation of the approximate strength of solutions (at 15°) which generally contain free sulphuric and some nitric acid as impurities, Wolff has prepared the following table:—

Per cent. $\text{Fe}_2(\text{SO}_4)_3$ .	Spec. grav.	Per cent. $\text{Fe}_2(\text{SO}_4)_3$ .	Spec. grav.
5	1.0426	35	1.3732
10	1.0854	40	1.4506
15	1.1324	45	1.5298
20	1.1825	50	1.6148
25	1.2426	55	1.7050
30	1.3090	60	1.8006

For the accurate estimation of the content of iron, a weighed quantity (about 1 g.) of the solution is diluted with water and sulphuric acid, the ferric salt reduced with zinc, and the cooled solution titrated with permanganate. In another small quantity of the substance the sulphuric acid is determined gravimetrically, preferably by Lunge's method (*cf.* Vol. I., p. 274).

The presence of nitric acid in the salt is detected by heating with sulphuric acid indigo solution, which becomes discoloured. Ferrous sulphate is recognised by the blue coloration given with a solution of potassium ferrocyanide, freshly prepared from previously washed crystals. Other metals are tested for in the same way as described for ferrous sulphate.

**Iron Alum**,  $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 + 24\text{H}_2\text{O}$  (Ferric ammonium sulphate).—In its pure state, iron alum forms amethyst-coloured octahedra, which dissolve in three to four parts of cold water. The salt may contain small quantities of ferrous sulphate and of nitric acid from its preparation; in dyeing, it is used in such cases as require a neutral ferric salt.

The corresponding potassium salt crystallises in colourless octahedra, and is used for the same purposes, but much less frequently.

**Ferric Nitrate** solution of a dark reddish brown colour is likewise used commercially as an "iron mordant" in dyeing. The strength of pure solutions may be determined by their specific gravity. The preparation generally contains considerable quantities of ferric sulphate. The content of iron and sulphuric acid are determined by the methods given for ferric sulphate. For the estimation of the nitric acid, a weighed, small quantity of the mordant is largely diluted with water, boiled with excess of sodium hydroxide, the filtrate from the ferric hydroxide precipitate evaporated, and the nitric acid in this solution converted into ammonia, and estimated by Ulsch's or other suitable method (*cf.* Vol. I., p. 311).

**Acetate of Iron**, prepared by dissolving iron turnings in crude acetic acid, comes into commerce as a greenish black solution, which smells strongly of wood tar, and contains the greater part of the iron as ferrous salt. Usually, only the specific gravity of this black mordant is taken ; this should be approximately 1.12 to 1.14.

**Ferric Chloride**,  $\text{Fe}_2\text{Cl}_6 + \text{aq.}$ , comes into commerce as a solid yellow mass, approximating to the formula  $\text{Fe}_2\text{Cl}_6 + 12\text{H}_2\text{O}$ , or as a dark brown solution. It is prepared by dissolving wrought iron in dilute hydrochloric acid, evaporating the solution to a sp. gr. of 1.3, and then oxidising with nitric acid. On further evaporating the concentrated solution, and then allowing to cool, the yellow solid ferric chloride is obtained.

The pure salt must dissolve in water to a clear solution ; potassium ferrocyanide should not give a blue coloration (ferrous chloride). The filtrate from the precipitation with ammonia in the hot solution should not be coloured blue (copper), and should give no precipitate with ammonium sulphide (copper, zinc, manganese). Free hydrochloric acid is recognised by the white fumes of ammonium chloride formed when a glass rod moistened with ammonia is brought near to a gently warmed concentrated solution ; free chlorine or nitrous acid in the solution produce a blue coloration, if iodide of zinc and starch paper be held close to the surface of the warmed solution. The content of iron is best determined by titration with stannous chloride solution (*cf.* p. 32). If the salt contains ferrous chloride, this is oxidised in a second sample with potassium chlorate, all the chlorine boiled off, and the solution titrated as before. The difference between this and the first determination of the iron gives the amount of iron present as ferrous chloride.

From the specific gravity of solutions of ferric chloride, the content of ferric chloride may be ascertained by means of the following table, prepared by Franz, for a temperature of  $17^\circ.5$  :—

Per cent. $\text{Fe}_2\text{Cl}_6$ .	Spec. grav.	Per cent. $\text{Fe}_2\text{Cl}_6$ .	Spec. grav.	Per cent. $\text{Fe}_2\text{Cl}_6$ .	Spec. grav.
2	1.015	22	1.175	42	1.387
4	1.029	24	1.195	44	1.412
6	1.044	26	1.216	46	1.437
8	1.058	28	1.237	48	1.462
10	1.073	30	1.257	50	1.487
12	1.086	32	1.278	52	1.515
14	1.105	34	1.299	54	1.544
16	1.122	36	1.320	56	1.573
18	1.138	38	1.341	58	1.602
20	1.154	40	1.362	60	1.632

*Potassium Ferrocyanide* (yellow prussiate of potash) and *Potassium Ferricyanide* (red prussiate of potash), *cf.* Vol. I., p. 555 ; *Sodium Ferrocyanide*, *cf.* Vol. I., p. 563.

ALUMINIUM SALTS (*cf.* Vol. I., pp. 608 *et seq.*)

## MANGANESE SALTS

**Manganese Sulphate, Manganese Chloride, and Manganese Acetate** find limited application in dyeing for the preparation of manganese bistre. The salts used for this purpose must be free from iron, which is readily verified; a small amount of calcium, which is always present, does not matter.

**Potassium Permanganate,  $\text{KMnO}_4$ .**—The pure salt crystallises in dark red rhombic needles which possess a greenish metallic lustre; it dissolves in fifteen parts of cold and in two parts of hot water. A product specially prepared for disinfection purposes comes into commerce as a green or dark red crumbly mass which contains potassium or sodium manganate and permanganate, oxides of manganese, free alkali, potassium and sodium nitrate, potassium chlorate, and potassium chloride.

The solution, acidified with sulphuric acid, is completely decolorised on warming with a little oxalic acid, and also on the addition of an aqueous solution of sulphur dioxide; on the further addition of an excess of ammonia and some ammonium sulphide, it gives a flesh-coloured precipitate of manganese sulphide. On warming the salt with dilute sulphuric acid, any chlorine present (chloride and chlorate) will be evolved, and is most easily recognised by means of potassium iodide and starch paper.

Sulphuric acid is precipitated in the usual way with barium chloride solution in a solution of the salt boiled with a large quantity of hydrochloric acid. The amount of potassium permanganate contained in the purer products is determined by titrating the very dilute solution with standard, acid ferrous sulphate.

**Sodium Permanganate,  $\text{NaMnO}_4$ .**—This salt is very soluble in water, has no tendency to crystallise, and comes into the market as a solid crumbly mass and in concentrated solutions. Both products are very impure (*cf.* above, Potassium Permanganate).

## CHROMIUM SALTS

**Potassium Chromate,  $\text{K}_2\text{CrO}_4$**  (yellow or neutral chromate of potassium, containing 51.49 per cent.  $\text{CrO}_3$ ).—The pure salt crystallises in citron yellow rhombic pyramids; its aqueous solution reacts slightly alkaline to litmus and neutral to phenolphthalein. It is insoluble in alcohol, and is partially decomposed in aqueous solution into potassium bichromate and potassium hydroxide. It sometimes contains large quantities of the isomorphous potassium sulphate as impurity; the



aqueous solution, strongly acidified with hydrochloric acid, then gives a precipitate with barium chloride of barium sulphate. For the quantitative estimation of these impurities, the aqueous solution, acidified slightly with hydrochloric acid, is precipitated with barium chloride, the precipitate washed by decantation and digested with hydrochloric acid and alcohol to dissolve the barium chromate. The content of chromic anhydride is determined by strongly acidifying an aqueous solution with sulphuric acid, reducing with an excess of ferrous ammonium sulphate, and titrating back the excess of ferrous sulphate in the very dilute solution with potassium permanganate (*cf.* p. 29).

According to Kremers, Schiff, and Gerlach, the specific gravities of aqueous solutions at 19°·5 are as follows :—

Per cent. K <sub>2</sub> CrO <sub>4</sub> .	Spec. grav.	Per cent. K <sub>2</sub> CrO <sub>4</sub> .	Spec. grav.	Per cent. K <sub>2</sub> CrO <sub>4</sub> .	Spec. grav.	Per cent. K <sub>2</sub> CrO <sub>4</sub> .	Spec. grav.
1	1·008	11	1·093	21	1·186	31	1·292
2	1·016	12	1·101	22	1·196	32	1·304
3	1·024	13	1·110	23	1·207	33	1·315
4	1·033	14	1·120	24	1·217	34	1·327
5	1·041	15	1·129	25	1·227	35	1·339
6	1·049	16	1·138	26	1·238	36	1·351
7	1·058	17	1·147	27	1·249	37	1·363
8	1·066	18	1·157	28	1·259	38	1·375
9	1·075	19	1·167	29	1·270	39	1·387
10	1·084	20	1·177	30	1·281	40	1·399

One hundred parts of water dissolve at :—

0° C.	Parts K <sub>2</sub> CrO <sub>4</sub> dissolved.	0° C.	Parts K <sub>2</sub> CrO <sub>4</sub> dissolved.	0° C.	Parts K <sub>2</sub> CrO <sub>4</sub> dissolved.
0	58·90	40	66·98	80	75·06
10	60·92	50	69·00	90	77·08
20	62·94	60	71·02	100	79·10
30	64·96	70	73·04		

**Sodium Chromate**, Na<sub>2</sub>CrO<sub>4</sub> + 10H<sub>2</sub>O.—This salt, which is very soluble in water, crystallises out in yellow needles on cooling a solution evaporated down to a sp. gr. of 1·56; the crystals are separated from the adhering mother liquor centrifugally. The salt deliquesces rapidly and liquefies. Alkali sulphates and carbonates are the chief impurities. The content of chromic anhydride is estimated by titration as described on p. 322.

**Potassium Bichromate**, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (red or acid chromate of potassium, containing 68·00 per cent. of CrO<sub>3</sub>).—This salt comes into commerce as fine yellowish red triclinic crystals which are usually contaminated with some potassium sulphate, and which also leave a small insoluble residue on solution in water. It is fusible, like the

neutral salt, at a red heat, and at a very high temperature is decomposed into the neutral salt, chromium oxide, and oxygen. The solid salt and its aqueous solution are very poisonous and cauterise strongly. It is insoluble in alcohol.

According to Alluard, one hundred parts of water dissolve at :—

0° C.	Parts $K_2Cr_2O_7$ dissolved.	0° C.	Parts $K_2Cr_2O_7$ dissolved.	0° C.	Parts $K_2Cr_2O_7$ dissolved.
0	4.6	40	25.9	80	68.6
10	7.4	50	35.0	90	81.1
20	12.4	60	45.0	100	94.1
30	18.4	70	56.7		

The following strengths of solutions and specific gravities at 19°.5 are given by Kremers and Gerlach :—

Per cent. $K_2Cr_2O_7$ .	Spec. grav.	Per cent. $K_2Cr_2O_7$ .	Spec. grav.	Per cent. $K_2Cr_2O_7$ .	Spec. grav.
1	1.007	6	1.043	11	1.080
2	1.015	7	1.050	12	1.087
3	1.022	8	1.056	13	1.095
4	1.030	9	1.065	14	1.102
5	1.037	10	1.073	15	1.110

The commercial product is guaranteed to contain from 67.5 to 68.0 per cent. of chromic anhydride; the chromic anhydride is determined volumetrically and the sulphuric acid gravimetrically, as described on p. 363.

**Sodium Bichromate**,  $Na_2Cr_2O_7$  (containing 76.36 per cent.  $CrO_3$ ).—The pure salt comes on to the market as red triclinic prisms which crystallise with two molecules of water; they are very hygroscopic, liquefy easily, melt at just over 100°, and lose their water of crystallisation at this temperature. It is sold in large quantities, however, in a dehydrated condition as a friable mass or in cakes containing sodium sulphate and insoluble carbonaceous matter, etc., as impurities; the content of chromic anhydride should amount to from 73 to 74 per cent.

Pure aqueous solutions have the following specific gravities and percentages of sodium bichromate :—

Per cent. $Na_2Cr_2O_7$ .	Spec. grav.	Per cent. $Na_2Cr_2O_7$ .	Spec. grav.
1	1.007	30	1.208
5	1.035	35	1.245
10	1.071	40	1.280
15	1.105	45	1.313
20	1.141	50	1.343
25	1.171		

**Chromium Fluoride**,  $\text{Cr}_2\text{F}_6 + 8\text{H}_2\text{O}$ .—The fluoride and its double salts are readily dissociated in aqueous solution with separation of chromium hydroxide,  $\text{Cr}(\text{OH})_3$ ; they have now been used for some years as mordants in the dyeing industry and in printing.

The fluoride comes on to the market as a dark green powder, stable in air; it is dissolved in water in wooden or copper vessels.

**Chromium Acetate, Chromium Chloride, Chromic Sulphate, etc.**, also find extensive application as chromium mordants in dyeing, etc.

**Chrome Alum**,  $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 + 24\text{H}_2\text{O}$  (containing 15.24 per cent.  $\text{Cr}_2\text{O}_3$ , 9.43 per cent.  $\text{K}_2\text{O}$ , and 32.06 per cent.  $\text{SO}_3$ ).—This salt forms large octahedra, which appear black by reflected light and dark violet by transmitted light. One hundred parts of water dissolve about twenty parts, producing a bluish violet coloured solution; on boiling, the solution turns green, and on evaporation, crystals are only formed after the concentrated, cold solution has stood for some time. Chrome alum is produced in large quantities as a by-product when a mixture of potassium chromate and sulphuric acid is used for oxidising purposes, *e.g.*, in the manufacture of anthraquinone.

The content of chromic oxide is determined by oxidising it to chromic anhydride, which is titrated. The solution is made alkaline with potassium or sodium hydroxide, small quantities of sodium peroxide added from time to time, the excess of peroxide removed by warming and passing in carbon dioxide, the cooled solution then strongly acidified with sulphuric acid, and the chromic anhydride estimated volumetrically as described on p. 322. The presence of potassium sulphate as impurity is ascertained by the usual determination of sulphuric acid, and by the estimation of the loss (water) on moderate ignition.

## ZINC SALTS

**Zinc Sulphate**,  $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ .—In the pure state this salt forms colourless, rhombic crystals having a glass-like lustre, which rapidly effloresce in dry air, and on quickly heating, dissolve in their water of crystallisation. It crystallises from solution at  $30^\circ$  with six molecules of water. On heating the salt to a little over  $100^\circ$ , it loses six molecules of water, whilst the last molecule is only driven off by gentle ignition.

On strongly igniting, zinc sulphate is decomposed into zinc oxide, sulphur dioxide, and oxygen. The crude salt comes on to the market in cakes or in the form of cones, prepared by fusing the crystals.

The most frequent impurity is manganese sulphate; less frequently it may contain small quantities of the sulphates of copper, iron, calcium, magnesium, and cadmium. Manganese and iron are separated by adding excess of ammonia to the aqueous solution of the salt; on standing with access of air, they are precipitated as hydroxides.



Copper and cadmium are precipitated by passing sulphuretted hydrogen through the aqueous solution acidified with sulphuric acid. The negligible impurities of calcium and magnesium sulphates do not interfere in any way with the technical uses of the salt.

One hundred parts of water dissolve at :—

° C.	Parts.		° C.	Parts.	
	ZnSO <sub>4</sub> dissolved.	ZnSO <sub>4</sub> +7H <sub>2</sub> O dissolved.		ZnSO <sub>4</sub> dissolved.	ZnSO <sub>4</sub> +7H <sub>2</sub> O dissolved.
0	43·02	115·22	60	74·20	313·48
10	48·36	138·21	70	79·25	369·36
20	53·13	161·49	80	84·60	442·62
30	58·40	190·90	90	89·78	533·02
40	63·52	224·05	100	95·03	653·59
50	68·75	263·84			

Specific gravity and strength of solutions at 15° :—

Per cent. ZnSO <sub>4</sub> +7H <sub>2</sub> O.	Spec. grav.	Per cent. ZnSO <sub>4</sub> +7H <sub>2</sub> O.	Spec. grav.
5	1·029	35	1·231
10	1·059	40	1·271
15	1·091	45	1·310
20	1·124	50	1·352
25	1·167	55	1·399
30	1·193	60	1·445

**Zinc Chloride, ZnCl<sub>2</sub>.**—The anhydrous chloride is a transparent white mass of sp. gr. 2·75 (butter of zinc), which is very hygroscopic, very soluble in water and in alcohol, melts at 100°, and distils at a red heat. It withdraws the elements of water from organic substances and carbonises wood ; its concentrated aqueous solution converts paper into parchment paper and reacts as a powerful caustic. It comes into commerce in sticks, which are generally only tested for their solubility in water (freedom from oxychloride). The concentrated aqueous solutions of zinc chloride, which are also commercial products, are tested for free acid (decolorisation of ultramarine paper) and specific gravity.

According to Krämer, the strength and specific gravity of aqueous solutions at 19°·5 are as follows :—

Per cent. ZnCl <sub>2</sub> .	Spec. grav.	Per cent. ZnCl <sub>2</sub> .	Spec. grav.
5	1·045	35	1·352
10	1·091	40	1·420
15	1·137	45	1·488
20	1·186	50	1·566
25	1·238	55	1·650
30	1·291	60	1·740

**Zinc Acetate**,  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 + 2\text{H}_2\text{O}$ , is very readily soluble in water, and is used as a mordant in dyeing. It is tested for impurities in the same way as zinc sulphate.

### COPPER SALTS

**Copper Sulphate**,  $\text{CuSO}_4 + 5\text{H}_2\text{O}$ .—The salt comes on to the market as large, bright blue, transparent, triclinic crystals, which in dry air become superficially effloresced. As impurities it most frequently contains ferrous sulphate, less frequently considerable quantities of zinc and nickel sulphates; it invariably contains traces of bismuth, arsenic, and antimony. Usually only iron is tested for, by saturating an aqueous solution with ammonia. For an accurate analysis, Hampe's method for the Analysis of Commercial Copper (pp. 192 *et seq.*) is recommended. If the copper is separated electrolytically out of a weighed quantity (3 to 5 g.) of the salt, the presence of appreciable quantities of arsenic and antimony can be recognised (*cf.* p. 166).

On heating to about  $200^\circ$ , copper sulphate loses all its water of crystallisation and yields a white, very hygroscopic powder, insoluble in alcohol. According to Poggiale, one hundred parts of water dissolve at:—

10°	20°	40°	80°	100°	
36.9	42.3	56.9	118.0	203.3	parts $\text{CuSO}_4 + 5\text{H}_2\text{O}$
20.9	23.5	30.3	53.1	75.3	„ $\text{CuSO}_4$ .

Strength and specific gravity of solutions at  $15^\circ$ :—

Per cent. $\text{CuSO}_4 + 5\text{H}_2\text{O}$ .	Spec. grav.	Per cent. $\text{CuSO}_4 + 5\text{H}_2\text{O}$ .	Spec. grav.	Per cent. $\text{CuSO}_4 + 5\text{H}_2\text{O}$ .	Spec. grav.
1	1.007	10	1.069	19	1.144
2	1.013	11	1.076	20	1.152
3	1.020	12	1.084	21	1.160
4	1.027	13	1.091	22	1.169
5	1.033	14	1.096	23	1.177
6	1.040	15	1.114	24	1.185
7	1.048	16	1.121	25	1.193
8	1.055	17	1.129		
9	1.062	18	1.137		

**Copper Chloride**,  $\text{CuCl}_2$  (crystallised,  $\text{CuCl}_2 + 2\text{H}_2\text{O}$ ).—This salt is generally only tested for the presence of iron, as in the case of copper sulphate, and the content of copper determined either by titrating the hot hydrochloric acid solution with stannous chloride or by means of the iodide method (pp. 175 *et seq.*). Salts of the alkalis (sodium chloride, etc.) present as impurities are detected by precipitating the aqueous solution of the salt with sulphuretted hydrogen and evaporating the filtrate from the copper sulphide. The pure hydrated salt forms beautiful green rhombic prisms or needles. The anhydrous chloride

obtained by heating the hydrated salt above  $100^{\circ}$  forms a brown, very hygroscopic mass; it is readily soluble both in water and alcohol.

According to Franz, aqueous solutions at  $17^{\circ}5$  have the following specific gravities and strengths:—

Per cent. CuCl <sub>2</sub> .	Spec. grav.	Per cent. CuCl <sub>2</sub> .	Spec. grav.	Per cent. CuCl <sub>2</sub> .	Spec. grav.
2	1·018	16	1·170	30	1·362
4	1·036	18	1·195	32	1·395
6	1·055	20	1·222	34	1·429
8	1·073	22	1·250	36	1·462
10	1·092	24	1·278	38	1·495
12	1·118	26	1·306	40	1·528
14	1·144	28	1·334		

**Copper Nitrate**,  $\text{Cu}(\text{NO}_3)_2 + 6\text{H}_2\text{O}$ .—The compound containing six molecules of water of crystallisation, which is obtained at a low temperature, melts at about  $30^{\circ}$ , and forms light blue tabular crystals; at a slightly higher temperature, dark blue prismatic crystals of the salt are obtained, containing three molecules of water of crystallisation which melt at  $115^{\circ}$ . Both salts are readily soluble in water and in alcohol, and are very hygroscopic.

The following substances occur as impurities:—Nitrates of lead, zinc, and sodium, and sulphates of copper and sodium. The commercial product, not intentionally adulterated, may contain up to 7 per cent. of impurities.

Lead may be separated and estimated as sulphate by evaporating the solution with excess of sulphuric acid; the copper is deposited electrolytically in the filtrate from the lead sulphate, and, in the solution from the copper, the zinc is precipitated as zinc sulphide with sulphuretted hydrogen, after neutralising with ammonia. The filtrate from the zinc sulphide is evaporated, the ammonium salts driven off, and the calcium, magnesium, and alkali salts determined in the ignited residue. For the estimation of the sulphuric acid, a separate portion is repeatedly evaporated with hydrochloric acid, and the diluted, hot hydrochloric acid solution precipitated with barium chloride solution.

**Copper Acetate**,  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$  (Crystallised Verdigris).—The dark bluish green crystals which come on the market are generally very pure and only contain an extremely small quantity of iron as impurity. It is tested for purity in the same way as copper sulphate.

## LEAD SALTS

**Lead Acetate**,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$  (Sugar of Lead).—The pure white sugar of lead crystallises in colourless plates or columns, which effloresce in dry air and gradually lose water and some acetic acid and



take up carbon dioxide. The freshly prepared salt dissolves completely in water to a clear solution; the solution of the effloresced salt is milky owing to the presence of lead carbonate, which is dissolved up by the addition of a few drops of acetic acid. At  $75^{\circ}$  the salt melts, at  $100^{\circ}$  it becomes anhydrous and solid, and again melts at  $280^{\circ}$ . One part of the salt dissolves in one and a half parts of water at  $15^{\circ}$ , in one part at  $40^{\circ}$ , and in one-half part at  $100^{\circ}$ . Alcohol dissolves about one-eighth of its weight of the salt; it is insoluble in ether. If the solution is precipitated with sulphuretted hydrogen, the filtrate from the lead sulphide should leave no residue on evaporation (iron). Copper is tested for by precipitating a concentrated aqueous solution of the salt with sulphuric acid and adding excess of ammonia to the evaporated filtrate from the lead sulphate.

*Brown Sugar of Lead.*—This product, prepared from crude pyrolignous acid and litharge, comes on to the market in a fused condition as irregular lumps. The content of lead is estimated by precipitating a solution of the salt with sulphuric acid.

The content of acetic acid in lead acetate and in lead vinegar is determined, according to Salomon, by making the solutions strongly alkaline in presence of phenolphthalein by means of standard potassium hydroxide solution, and titrating back the excess with a standard solution of acetic acid of equal strength, till the disappearance of the red colour. The difference gives the acetic acid in combination with the lead. Lead vinegar is first acidified with standard acetic acid, excess of potassium hydroxide solution then added, and the excess titrated back with acetic acid.

Fresenius adds a measured small excess of sulphuric acid to a solution of 5 g. of lead acetate in water in a 250 c.c. flask, swirls the contents of the flask round, fills up to the mark, adds further a volume of water corresponding to the precipitated lead sulphate (sp. gr. 6.3), shakes, and filters through a dry filter paper. The sulphuric acid, in a fifth of the filtrate (50 c.c.), is precipitated with barium chloride, the barium sulphate weighed, and the content of lead in the acetate calculated from the sulphuric acid used for the precipitation of the lead. Further portions of 50 c.c. are titrated with normal alkali, the sulphuric acid deducted, and the content of acetic acid in the lead acetate thereby ascertained.

**Lead Nitrate**,  $\text{Pb}(\text{NO}_3)_2$ .—The salt comes into commerce as colourless or white regular crystals (octahedra and combinations of octahedra and cube), which seldom contain any appreciable quantity of impurities. It is fairly soluble in water; a solution saturated at  $20^{\circ}$  (sp. gr. 1.415) contains 37 per cent. of lead nitrate. Dilute nitric acid and 90 per cent. alcohol dissolve it but very slightly; it is insoluble in strong nitric acid and in absolute alcohol.

In order to test for impurities, the lead is converted into sulphate by evaporation with excess of sulphuric acid and any residue obtained on evaporating the filtrate from the lead sulphate is examined for copper, iron, and calcium.

**Lead Sulphate,  $\text{PbSO}_4$ .**—Crude lead sulphate is obtained in large quantities as a by-product in the preparation of aluminium acetate and ferric acetate solutions for calico printing, and is chiefly bought up by lead works. Smaller quantities are worked up into lead colours (white lead, chrome yellow, red lead). It comes on to the market as a brown-coloured mass containing water; the colour arises from the lead-vinegar used for the decomposition of the alum or iron alum. The examination is usually limited to the determination of the lead. An average sample of several grams is dissolved in a hot, concentrated solution of ammonium acetate, the solution filtered, and pure lead sulphate precipitated from the diluted filtrate by means of sulphuric acid. In lead works the product is assayed in the dry way, by fusing with potassium carbonate, argol, and iron (*cf.* Assay of Lead, pp. 220 *et seq.*).

#### TIN SALTS

**Stannous Chloride,  $\text{SnCl}_2 + 2\text{H}_2\text{O}$  (Tin Salt).**—The commercial product consists of colourless or pale yellowish white crystals possessing a fatty appearance, which are freed from the adhering mother liquor centrifugally. It usually only contains the impurities arising from the tin and hydrochloric acid used in its preparation, in small quantities; it is seldom adulterated with magnesium or zinc sulphate.

The salt only dissolves completely in a little water and in absolute alcohol, when freshly prepared. If exposed to the air for any length of time, the oxychloride is formed, which is insoluble in water; on heating with hydrochloric and tin, this is again converted into stannous chloride.

On largely diluting an aqueous solution of the salt, considerable separation of the oxychloride,  $\text{Sn}(\text{OH})\text{Cl}$ , takes place; solutions containing hydrochloric acid, ammonium chloride, or tartaric acid remain clear. The solid salt and its solutions rapidly absorb oxygen from the air.

The content of stannous chloride is estimated by one of the volumetric methods described on p. 266.

The presence of lead, copper, zinc, and iron, as impurities, is detected by adding excess of ammonia to a solution of the salt, and warming for some time with a considerable quantity of yellow ammonium sulphide, when the above metals remain undissolved as sulphides. Sulphates produce a precipitate of barium sulphate in a largely diluted hydrochloric acid solution. According to Merz, zinc and magnesium sulphates remain undissolved as minute crystalline deposits, if several grams of the salt are stirred with five times their

weight of absolute alcohol; any tin oxychloride which may be present remains undissolved as a flocculent residue.

The strength of aqueous solutions containing hydrochloric acid may be approximately estimated from their specific gravity. Gerlach has drawn up the following table for solutions at 15°:—

Per cent. SnCl <sub>2</sub> +2H <sub>2</sub> O.	Spec. Grav.	Per cent. SnCl <sub>2</sub> +2H <sub>2</sub> O.	Spec. Grav.	Per cent. SnCl <sub>2</sub> +2H <sub>2</sub> O.	Spec. Grav.	Per cent. SnCl <sub>2</sub> +2H <sub>2</sub> O.	Spec. Grav.
2	1·013	22	1·161	42	1·352	62	1·613
4	1·026	24	1·177	44	1·374	64	1·644
6	1·040	26	1·194	46	1·397	66	1·677
8	1·054	28	1·212	48	1·421	68	1·711
10	1·068	30	1·230	50	1·445	70	1·745
12	1·083	32	1·249	52	1·471	72	1·783
14	1·097	34	1·268	54	1·497	74	1·821
16	1·113	36	1·288	56	1·525	75	1·840
18	1·128	38	1·309	58	1·554		
20	1·144	40	1·330	60	1·582		

**Stannic Chloride, SnCl<sub>4</sub>.**—The pure liquid compound finds its way but seldom into commerce; it occurs much more frequently as a hydrated salt-like mass containing sodium chloride, and as concentrated solutions. In the dyeing industry solutions of tin in aqua regia are called tin nitrate, tin composition, tin solution, physic, scarlet composition, rosing salt, etc., and are usually contaminated with free nitric acid, ferric chloride, zinc chloride, salt and stannous chloride, or contain, in the case of the three latter products, intentional additions of such salts. The chloride combines with five molecules of water of crystallisation to form a white salt, which is used for the same purposes as the other preparations.

The presence of stannous chloride is recognised by the separation of mercurous chloride (calomel) on the addition of a solution of mercuric chloride; copper, lead, zinc, and iron remain as sulphides on treatment with ammonia and ammonium sulphide. Salts of the alkalis, together with zinc and iron salts, are detected on evaporating the filtrate after the precipitation of the tin by sulphuretted hydrogen. The presence of nitric acid is shown by the addition of a crystal of ferrous sulphate, when the liquid in the immediate neighbourhood of the crystal is coloured red.

The total content of tin is determined by immersing a strip of pure, stout zinc foil in a solution of the salt for about twelve hours, removing the precipitated tin with a brush, washing, dissolving in a hot ferric chloride solution, and titrating the ferrous chloride formed. Or, the tin may be dissolved in hydrochloric acid and the solution titrated by means of ferric chloride. The stannous chloride is titrated in a separate sample by the same method, and the stannic chloride in the salt thus estimated from the difference between the two determinations.

If the solution of stannic chloride does not contain too much



impurity, its strength may be estimated approximately from its specific gravity. For this purpose the following table by Gerlach for a temperature of  $15^{\circ}$  may be employed:—

Per cent. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ .	Spec. Grav.	Per cent. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ .	Spec. Grav.
5	1.030	45	1.320
10	1.059	50	1.366
15	1.091	55	1.416
20	1.124	60	1.468
25	1.158	65	1.526
30	1.195	70	1.587
35	1.235	80	1.727
40	1.276	90	1.893

**Tin Ammonium Chloride**,  $\text{SnCl}_4 \cdot 2\text{NH}_4\text{Cl}$  (Pink Salt).—This salt forms beautiful white crystals, which dissolve readily in water. The content of tin is tested for (as above), since the salt frequently contains an excess of ammonium chloride. It is much used in dyeing as a substitute for the more strongly corrosive stannic chloride.

**Sodium Stannate**,  $\text{Na}_2\text{SnO}_3 + 3\text{H}_2\text{O}$  (Preparing Salts).—The pure salt forms colourless crystals; the ordinary commercial product is usually largely contaminated with sodium carbonate and hydroxide, and not infrequently also contains arsenic. The content of tin is determined by precipitation with zinc, dissolving the washed tin in hydrochloric acid, and titrating. Arsenic is tested for in a simple Marsh apparatus.

## SILVER AND GOLD SALTS

**Silver Nitrate**,  $\text{AgNO}_3$  (Lunar Caustic).—The pure salt crystallises in large colourless rhombic plates, which, in presence of dust, blacken in the light. At  $218^{\circ}$  the nitrate melts and solidifies to a crystalline, radiating mass. It is readily soluble in water and in alcohol. One hundred parts of water dissolve at:—

$0^{\circ}$	$19.5^{\circ}$	$54^{\circ}$	$85^{\circ}$	$100^{\circ}$
121.9	227.3	500	714	1111 parts of $\text{AgNO}_3$ .

The pure salt dissolves to a perfectly clear solution in water; the colourless solution should not become turbid (lead, bismuth) or coloured blue (copper) on the addition of a large excess of ammonia.

The content of silver is determined gravimetrically as silver chloride, and volumetrically by titration with ammonium thiocyanate according to Volhard's method (p. 116). The salt, as it comes on to the market in the form of sticks for surgical purposes, cannot be distinguished in appearance from that fused with potassium nitrate which is prepared for a similar purpose. The content of nitre is either calculated by difference from the result of the silver determination, or the filtrate from the

silver chloride is evaporated and the potassium chloride in the residue determined and calculated to potassium nitrate. The presence of potassium nitrate may be recognised by moistening a strip of filter paper with the aqueous solution, drying and igniting, the residue being strongly alkaline.

**Gold Chloride**,  $\text{AuCl}_3$ , forms a yellowish brown deliquescent mass, which dissolves readily in water, alcohol and ether, producing solutions of a yellowish red colour.

**Chlor-auric Acid**,  $\text{HAuCl}_4 + 4\text{H}_2\text{O}$ , crystallises in long yellow needles. On carefully heating in a covered porcelain crucible to a bright red heat, both salts leave a residue of pure gold; the pure chloride,  $\text{AuCl}_3$ , gives 64.96 per cent. Au, and the hydrochloric acid compound 47.85 per cent.

**Sodium Chlor-aurate**,  $\text{NaAuCl}_4 + 2\text{H}_2\text{O}$  (Gold Salt), crystallises in golden-yellow rhombic prisms, which effloresce readily. The percentage of gold is 49.5. It is very soluble in water.

**Potassium Chlor-aurate**,  $\text{KAuCl}_4 + 2\text{H}_2\text{O}$ , and **Ammonium Chlor-aurate**,  $2\text{NH}_4\text{AuCl}_4 + 5\text{H}_2\text{O}$ , are yellow salts which crystallise well and are used for the same purposes as "gold salt."

For the estimation of the gold, a small weighing of the salt is mixed with half its weight of sodium carbonate, and gradually heated to a dull red heat in a covered porcelain crucible. When cold, the salt is dissolved in hot water, and the gold dried, ignited, and weighed. Copper is the only impurity, and occurs in traces. For its determination, the gold is precipitated from the hydrochloric acid solution of the gold salt by warming with pure ferrous sulphate, and sulphuretted hydrogen then passed into the filtrate for some time to precipitate the copper.

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# ARTIFICIAL MANURES

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## I.—GENERAL METHODS OF EXAMINING ARTIFICIAL MANURES

### I. ESTIMATION OF NITROGEN

#### A. TOTAL NITROGEN BY KJELDAHL'S METHOD.

It has long been established that Kjeldahl's method of estimating nitrogen<sup>1</sup> gives accurate results with all substances, the nitrogen of which can be estimated by the soda-lime method; hence the latter method has accordingly been replaced by that of Kjeldahl in practically all laboratories.

The method, as originally devised, has been so altered, improved, and simplified, that Stutzer proposed some time back to call it the "Sulphate Method" in contradistinction to the soda-lime method, since it is impossible to exactly designate the present method by adding to the name of Kjeldahl all those who have co-operated in the improvements. In spite, however, of the various changes introduced the principle has remained the same, viz., the conversion of all the organic nitrogen into ammonium sulphate by boiling with concentrated sulphuric acid, and the subsequent estimation of the ammonia by distillation with sodium hydroxide.

#### a. In Substances free from Nitric Acid.

Wilfarth's<sup>2</sup> modification of Kjeldahl's method is best suited to the estimation of nitrogen in ordinary substances not containing nitric acid. Wilfarth first observed that the time required for decomposition is considerably shortened by the addition of metallic oxides. The most suitable metals proved to be copper and mercury, and the best proportions are 0.5 g. anhydrous copper sulphate, or 0.7 g. metallic mercury,

<sup>1</sup> *Z. anal. Chem.*, 1883, 22, 366.

<sup>2</sup> *Chem. Zeit.*, 1875, 9, 286, 502.



or about 1 g. mercury oxide, to 1 g. substance. Mercury has the greatest effect on the oxidation, so that the decomposition requires appreciably less time than when copper sulphate is used. When mercury or mercuric oxide is used, however, it is necessary in the subsequent distillation of the ammonia to add sufficient potassium sulphide solution (about 25 c.c. of a solution of 40 g. potassium sulphide per litre) to the sodium hydroxide to precipitate the whole of the mercury as sulphide, whereby the liquid assumes a black appearance; also, granulated zinc should be added to prevent bumping. As Böttcher established some years ago,<sup>1</sup> addition of potassium sulphide is not necessary provided a rapid evolution of hydrogen is maintained within the liquid; this is effected by the addition of 1.5 g. of zinc dust (which, of course, must be free from nitrogen and low in oxide) to the contents of the flask before distillation. The mercury-ammonium compounds are easily and completely decomposed by nascent hydrogen, and the ammonia distils over just as quickly as when potassium sulphide and zinc are used. Having observed that, in the case of various difficultly decomposed substances, rich in nitrogen, such as horn meal, fish meal, etc., considerably more nitrogen is found when mercury is used than when copper sulphate is employed, Böttcher recommends the following procedure:—

One gram of the finely powdered substance is placed in a small flask of Bohemian glass of about 150 c.c. capacity, and one drop of mercury (about 1 g.) and 25 c.c. of acid, prepared by adding 200 g. of phosphorous pentoxide to 1 litre of concentrated sulphuric acid (sp. gr. 1.84), are added. (The mixture must always be tested for nitrogen.) The flask is then heated on a wire gauze, first with a small flame, and subsequently to vigorous boiling.

It is advisable to place the decomposition flasks in an inclined position on the gauze, so that the side, and not the bottom, receives the heat. For this purpose various forms of apparatus have been devised, which can accommodate fifteen to twenty flasks, and thus permit of fifteen to twenty estimations being carried on at the same time. The decomposition must take place in an efficient draught and in an ammonia-free atmosphere. It is advantageous to place the whole apparatus on a lead plate, the edges of which are bent up and in which is strewn a thick layer of sand, so that if a flask happen to crack during the heating, the boiling sulphuric acid will flow into the sand.

In the case of substances which froth up during decomposition, a little solid paraffin is added. To avoid the escape of acid fumes and loss of sulphuric acid by spitting, the flask is loosely closed by a device first recommended by Kreusler, viz., a glass stopper made by drawing out a wide glass tube into a long point, the lower end of which is fused

<sup>1</sup> *Landw. Versuchs-Stat.*, 1892, 41, 170.

up. The heating is continued until the contents of the flask are perfectly colourless. The time required to effect this varies with the nature of the substance, and will range from half an hour to two or three hours in the case of such substances as dried flesh, dried blood, etc. It is, therefore, desirable in the case of all substances which are difficultly decomposed, that the boiling should be continued for three hours for the sake of certainty. When cold, the contents of the flask are carefully washed into a distillation flask of 500 c.c. capacity, about 200 c.c. of water being used for this purpose, 100 c.c. sodium hydroxide solution of sp. gr. 1.28 (nitrogen-free), and 1 to 1.5 g. zinc dust added, and the ammonia distilled off into standard sulphuric acid.

The distillation can be carried out either with or without a condenser; in the latter case the lower end of the delivery tube must dip into the sulphuric acid. A method to be recommended is to distil the ammonia through cooled, tin tubes which are sufficiently narrow (5 to 6 mm. inner diameter) for the successive portions of the distillate to effect a continuous washing-out of the tubes; the end of the condenser tube is connected with an Erlenmeyer flask (300 to 400 c.c. capacity) by means of a glass tube. The flask should contain 20 c.c. of standard sulphuric acid, and should be provided with a small Will and Varrentrapp receiver. To prevent small quantities of sodium hydroxide from passing over into the condenser tube during distillation, a fairly large bulb-tube with the tube bent downwards is placed between the condenser and the distillation flask. When zinc dust is used even this does not suffice, and the receivers recommended by Kjeldahl must be used, which serve simultaneously as washing apparatus and receiver; but in this case the distillation must be interrupted once, to allow the water which collects in the receivers to flow back into the distillation flask.

In the case of substances which are difficult to obtain in a finely divided condition, correct average samples are obtained as follows:—Three to five grams are weighed out and boiled with 50 to 60 c.c. of sulphuric acid, and 2 to 3 g. of mercury. When cold, the liquid is washed into a graduated 300 c.c. flask, made up to the mark and thoroughly shaken; 100 c.c. are then distilled with sodium hydroxide and zinc dust.

After the distillation is complete, the excess of sulphuric acid is titrated back with dilute sodium hydroxide, using 2 c.c. of a solution of Congo red as indicator. The percentage of nitrogen is then calculated from the ammonia found. The Congo red solution is prepared by shaking 2 g. of Congo red with 500 c.c. of 50 per cent. alcohol, till the whole is dissolved; 500 c.c. of water are then added.

The decomposition of nitrogenous substances by sulphuric acid is very appreciably accelerated by adopting J. W. Gunning's<sup>1</sup> method of

<sup>1</sup> *Z. anal. Chem.*, 1889, 28, 188.

adding a fairly large quantity of potassium sulphate to the sulphuric acid. This has been tested by Böttcher, Atterberg, Arnold, Wedemeyer, and others, who have found it serviceable. Böttcher considers a mixture of 20 c.c. of phosphor-sulphuric acid, 1 g. of mercury, and 15 to 18 g. of potassium sulphate to be the best and most rapidly acting oxidation liquid. In the case of substances which do not froth, the potassium sulphate may be added with the sulphuric acid, but it is best to add the sulphate after the acid has boiled and the frothing ceased. The boiling is continued until the decomposition is complete and the liquid becomes colourless, the time occupied being usually about thirty minutes. The liquid can be diluted with water after standing five to ten minutes; it is then transferred to the distillation flask, and the ammonia distilled off as above.

#### b. In Substances containing Nitric Acid and in Saltpetre.

Kjeldahl's method as originally devised was not applicable to the quantitative determination of nitrogen in the case of all those substances which contain nitrogen in the form of nitrates, but it has been since established that it is generally applicable when suitable modifications are introduced.

For the estimation of the total nitrogen in substances containing nitrate, the following methods are suitable:—

**1. Jodlbaur's Method.**<sup>1</sup>—In this method the substances are decomposed by sulphuric acid containing phenol, whereby the nitrogen of the nitrate is combined as nitrophenol, which is then reduced by zinc dust to aminophenol; the nitrogen in the aminophenol is determined by the sulphate method in the usual way. Böttcher recommends the following procedure as the most advantageous:—The manure mixture containing nitrate is dried, 1 g. weighed out and transferred to a Bohemian glass flask of about 350 c.c. capacity, 30 c.c. of phenolsulphuric acid gradually added with constant shaking and cooling in cold water, the mixture allowed to stand for a half to one hour, and occasionally shaken round, until as much is dissolved as possible.

The phenolsulphuric acid solution contains 200 g. of phosphoric anhydride and 40 g. of phenol in 1 litre of concentrated pure sulphuric acid. It is best prepared by dissolving the phosphoric anhydride in part of the sulphuric acid, and the phenol in the remainder, and then mixing the two solutions after they have cooled.

From 2 to 3 g. of dry, nitrogen-free zinc dust are then very gradually added, the flask being again thoroughly shaken and well cooled, and one drop (= 1 g.) of mercury then added. If the mixture be sufficiently shaken and cooled, the zinc dust can be added continuously without any risk of loss. After standing for one to two hours the

<sup>1</sup> Landw. Versuchs-Stat., 1888, 35, 447.



decomposition flask is placed over a flame and cautiously heated to avoid frothing, and the contents boiled till clear and colourless. The liquid is then allowed to cool, poured into a distillation flask, and the ammonia distilled off as usual. Since 30 c.c. of phenolsulphuric acid are used for the decomposition, 110 c.c. of sodium hydroxide must be added for distillation.

If the substances under examination are moist, they must be rubbed up in a mortar with a little nitrogen-free plaster-of-Paris before adding the phenolsulphuric acid.

As an alternative, the following directions of Stutzer may be adopted:—Twenty to twenty-five c.c. of water are added to the substance in the decomposition flask, which is shaken round and placed in a drying oven at 100° to 110°, till all the water has evaporated. When cold, 30 c.c. of phenolsulphuric acid are added with cooling, then, after standing for half to one hour, 2 to 3 g. of zinc dust and one drop of mercury, and the rest of the estimation carried out as described above.

In examining potassium and sodium nitrate by this method, it is best to adopt the latter modification, using 0.5 g. of substance. To obtain a good average sample, 10 g. of saltpetre are dissolved in 500 c.c. of water, and 25 c.c. of this solution evaporated in the decomposition flask at 100° to 110°.

**2. Förster's Method.**<sup>1</sup>—Förster carried out a series of experiments, using, as others had previously done, phenolsulphuric acid, with or without the addition of reducing agents. In these experiments he always found losses of 0.3 to 0.5 per cent. of nitrogen, which could not be otherwise explained than that small quantities of nitric acid escape the action of the phenolsulphonic acids, and volatilise during the subsequent heating. To avoid these losses, he proposed the addition of sodium thiosulphate, the revised method being carried out as follows:—

One-half gram of finely powdered saltpetre, or 1 g. of the manure mixture containing saltpetre, is placed in an ordinary decomposition flask, or, as an alternative, a larger quantity of the substance is dissolved in water, and an amount, corresponding to 0.5 g. of saltpetre, is evaporated to dryness in the decomposition flask; 15 c.c. of a (preferably) 6 per cent. phenolsulphuric acid solution are then added, and the whole shaken till the saltpetre is completely dissolved. One to two grams of sodium thiosulphate are next added, and when decomposed, 10 c.c. of pure sulphuric acid and about 1 g. of mercury. This solution is boiled in the usual way till the liquid is colourless, and the ammonia then distilled off.

The sodium thiosulphate must not be added before the phenolsulphuric acid, since the very energetic reaction which ensues would

<sup>1</sup> *Chem. Zeit.*, 1889, 13, 229.

cause a considerable loss of nitrogen. The results are influenced when the phenolsulphuric acid contains more than 7 per cent. or less than 4 per cent. of phenol. Cooling, as in the Jodlbaur method, is not necessary, either on dissolving the nitrate in the phenolsulphuric acid, or on adding the sodium thiosulphate. The oxidation of organic substances is generally complete in one and a half hours.

This process is more convenient, and gives more reliable results than the more tedious method of Jodlbaur, and is, therefore, to be recommended in preference to the latter, especially as Jodlbaur's method affords correct figures only when the conditions are exactly and minutely carried out. Further, in Förster's method, bumping is avoided during the subsequent distillation, as no difficultly soluble sulphate is formed.

**3. G. P. Veitsch's<sup>1</sup> Modification of Gunning's Method.**—In this method the nitrate is placed in the distillation flask, and 35 to 40 c.c. of sulphuric acid added, which contains 34 g. of salicylic acid per litre. The mixture is allowed to stand at the ordinary temperature till the nitrate has dissolved, 6 to 7 g. of finely powdered potassium sulphate are then added, and the flask heated for fifteen minutes over a small flame, then over a full flame until the mixture is clear. When cold, the ammonia is distilled off as usual.

## B. NITROGEN COMBINED AS AMMONIA

The nitrogen combined as ammonia in commercial ammonium salts and in ammoniacal fertilisers is estimated by distillation with freshly ignited magnesia (about 3 g. magnesia to 1 g. ammonia), which must be as free from carbonate as possible. If the substance under examination contain no easily decomposable organic nitrogen compounds together with the ammonia-nitrogen, the distillation can be carried out with sodium hydroxide. If sodium hydroxide be used to titrate back the sulphuric acid, with either Congo red or methyl orange as indicator, the results will not be influenced by the carbonic acid in the magnesia.

To carry out the method, 20 g. of the substance to be examined are dissolved in a litre of water, 25 c.c. of this solution (=0.5 g. substance) transferred to the distillation flask, used in Kjeldahl's method, by means of a pipette, the whole diluted with 150 c.c. of water, and about 3 g. of ignited magnesia added. The flask is then connected at once to the condenser tube, shaken round, and about 100 c.c. of the solution distilled off; the evolved ammonia is collected in standard sulphuric acid as usual, and the excess of acid is titrated back with sodium hydroxide.

Ammonia-nitrogen can also be estimated volumetrically by means

<sup>1</sup> *J. Amer. Chem. Soc.*, 1899, 21, 1094.

of Knop's Azotometer, which yields very reliable results when the experiments are efficiently conducted (*cf.* Vol. I., p. 125).

C. NITROGEN COMBINED AS NITRATE (*cf.* Vol. I., p. 309)

**1. The Schlösing-Grandeau-Wagner Method.**<sup>1</sup>—The estimation is carried out in a small flask of 250 to 300 c.c. capacity, closed by a double-bored rubber stopper, fitted with a 15 c.c. funnel, provided with glass tap; the lower end of the tube of the tap-funnel is drawn out to a fine point, and reaches into the body of the flask, but not into the liquid. A delivery-tube is fitted through the second opening in the stopper, the end of which is placed in a glass dish, filled with air-free water. A tube, graduated to 0.1 c.c., and provided with a glass tap at its upper end, is supported above the dish.

To carry out the estimation 40 c.c. of ferrous chloride solution containing about 200 g. of iron, and an equal weight of 20 per cent. hydrochloric acid per litre, are placed in the flask, a few cubic centimetres of hydrochloric acid poured into the funnel, the tap opened, and the air in the tube of the funnel driven out by allowing the acid to flow down. The contents of the flask are then boiled. As soon as all the air is driven out of the flask, the 100 c.c. graduated tube is filled with water and inverted over the delivery tube. Ten c.c. of a nitrate solution, containing exactly 33 g. of pure sodium nitrate per litre, are then poured into the funnel, and the tap adjusted so that the solution drops slowly into the continuously boiling iron solution. When nearly all the solution has run in, the funnel is rinsed round twice with 20 per cent. hydrochloric acid, which is similarly allowed to flow, drop by drop, into the boiling iron solution. The decomposition is complete when no more nitric oxide is evolved. The graduated tube is now set aside, a second substituted for it, and—without the ferrous chloride having once ceased boiling—10 c.c. of the unknown nitrate solution (saltpetre or manure mixture containing saltpetre) are poured into the funnel. This solution must be of such a concentration that 50 to 90 c.c. of nitric oxide are evolved. The end of the reaction is easily recognised by the complete condensation of the vapours entering the delivery tube. When this takes place the funnel is again twice rinsed with hydrochloric acid. Six or seven consecutive estimations can thus be similarly carried out without renewing the iron solution. Finally, a second control experiment is made with 10 c.c. of the standard nitrate solution. Air is then allowed to enter the flask by opening the tap full, the flame is removed, and the apparatus supplied with fresh iron solution for further estimations.

<sup>1</sup> *Chem. Zeit.*, 1884, 8, 37; *Cf.* Vol. I., p. 317, and this Vol., p. 499.



The graduated tubes containing the nitric oxide are meanwhile transferred with the help of small dishes, filled with water and held beneath the tubes, to a high glass cylinder filled with water. The tubes are supported by brass clamps on the rim of the cylinder. The cylinder is provided with an overflow tube. When the several graduated tubes in the cooling cylinder have attained the same temperature, the volumes of nitric oxide gas are read off, with the water at the same level inside and outside the tubes, and the volume of gas calculated, without further temperature or pressure measurements being necessary.

This method, although requiring some analytical skill, is very simple, and is particularly to be recommended where numerous nitrate estimations have to be carried out consecutively.

*Calculation.*—In the case of Chili saltpetre, 33 g. are made up to one litre, and 10 g. of this solution used for the estimation. With the help of Grandeau's tables the percentage of nitrogen in the nitrate can be ascertained directly from the volume of nitric oxide obtained. If these tables are not available the percentage can be calculated as follows:—If 10 c.c. of the standard nitrate solution evolved 90.0 c.c. nitric oxide gas, and 10 c.c. of the nitrate under examination evolved 86.1 c.c., then the latter contains  $\frac{86.1 \times 100}{90.0} = 95.67$  per cent. sodium nitrate, or  $\frac{95.67 \times 14.01}{85.01} = 15.77$  per cent. nitrogen.

In the case of manure mixtures containing nitrate, 33 g. of substance are similarly dissolved in one litre of water, and either 10, 20, or 30 c.c. of the filtrate used for the estimation, so that at least 50 c.c. of nitric oxide gas are obtained.

**2. Ulsch's Method.**<sup>1</sup>—This is founded on the fact that, when a nitrate solution is warmed with dilute sulphuric acid and very finely divided iron (reduced in hydrogen), the nitric acid is very rapidly and completely reduced to ammonia, and can be estimated as such.

In a half litre flat-bottomed flask are placed 25 c.c. of an aqueous nitrate solution containing at the most 0.5 g. of potassium nitrate or an equivalent quantity of other nitrate. (In the case of Chili saltpetre, 25 c.c. of a solution containing 8 g. to 500 c.c. water.) Ten c.c. of dilute sulphuric acid of sp. gr. 1.35 (obtained by mixing about two volumes of water with one volume of concentrated sulphuric acid), and, lastly, 5 g. of commercial, reduced iron, are added. To avoid loss by spirting the flask may be closed by a small pear-shaped glass vessel, similar to Kreusler's glass stoppers, of about 25 c.c. capacity, which is filled with cold water, so that it also serves as a reflux condenser, but this is really unnecessary.

<sup>1</sup> This method, as modified by Böckmann, is fully described in Vol. I., p. 311.

A vigorous, but not violent, evolution of gas is brought about by cautious heating with a very small flame, which is gradually raised, so that the liquid begins to boil after a lapse of about four minutes from the beginning of the heating. After gently boiling for about half a minute the reduction should be complete; it thus requires nearly five minutes in all.

The contents of the flask are then diluted with 50 c.c. of water, made alkaline by adding 20 c.c. of sodium hydroxide solution of sp. gr. 1.25, the ammonia distilled over as usual, and collected in standard sulphuric acid. Addition of zinc before distillation is quite superfluous. Since the total volume of the liquid is very small, the whole of the ammonia will be driven over by about five to seven minutes' vigorous boiling.

This method has the great advantages of certainty and rapidity, and is better suited to separate estimations than those described above; it allows of a nitric acid estimation, exclusive of the preparation of substance and the titration of the ammonia, being carried out in fifteen to twenty minutes.

**3. König's Method.**<sup>1</sup>—Five grams of saltpetre are dissolved in a litre of water, and 100 c.c. of this solution (=0.5 g. saltpetre), or an equivalent amount of a solution made from other manures, are placed in a 500 to 600 c.c. flask, and 18 to 20 g. of potassium hydroxide (free from nitric acid), 75 c.c. of methylated spirit, and 8 to 10 g. each of zinc and iron dust, and finally, a few granules of pure animal charcoal, to prevent frothing, added. The flask is then connected to a Peligot U-shaped bulb tube, of about 200 c.c. capacity, containing 10 c.c. of normal sulphuric acid, placed in a vessel filled with cold water. To prevent the potassium hydroxide solution being carried over, the connecting tube must be provided with a bulb and be bent downwards. The flask is allowed to stand about three to four hours, until the vigorous evolution of hydrogen, which takes place at first, has subsided; the liquid is then distilled with a very small flame, so that the distillation occupies about two hours. Distillation is complete when the whole of the methylated spirit has passed over and water begins to distil; the water vapour collects in drops in the condenser tube and heats the neck of the receiver.

To obtain correct results it is necessary to follow these instructions accurately.

**4. The Zinc-Iron Method.**<sup>2</sup>—This method, suggested by E. Raab and described by Böttcher, is considerably more expeditious than the above; it is founded on the same principle as that of König. When a nitrate is heated in alkaline solution in which nascent hydrogen is

<sup>1</sup> *Die Untersuchung. landwirtschaftlich und gewerblich wichtiger Stoffe*, 3rd edition, 1906, p. 139.

<sup>2</sup> *Landw. Versuchs-Stat.*, 1892, 41, 370.

being evolved in sufficient quantity, the whole of the nitric acid is converted into ammonia. After various preliminary trials, the following method was adopted:—Ten grams of saltpetre, or manure mixture containing saltpetre, are dissolved in 500 c.c. of water; 25 c.c. of this solution (or in the case of mixed manures, 50 c.c.), corresponding to 0.5 g. (or 1 g.) of substance, are placed with about 120 c.c. of water in the distillation flask (500 c.c. capacity) of Kjeldahl's apparatus. About 5 g. of nitrogen-free zinc dust, 5 g. of iron powder (reduced iron), and 80 c.c. of sodium hydroxide of sp. gr. 1.28 are added, the flask then connected with the rest of the apparatus, 20 c.c. of standard sulphuric acid having been placed in the receiver. The flask is allowed to stand for one to two hours with repeated shaking, and about 100 c.c. of the solution distilled off, and titrated as usual. The distillation must be begun with a very small flame; otherwise a too vigorous evolution of hydrogen may carry over some alkali. When Kjeldahl's adapters (p. 377) are used there is no risk of sodium hydroxide being carried over.

This method gives equally good results with pure saltpetre and with mixed manures of the most various kinds; its simplicity and low cost recommend its use in all laboratories in which numerous estimations of nitrate-nitrogen contained in saltpetres and saltpetre mixtures are required.

T. Schmitt<sup>1</sup> uses a 750 c.c. Erlenmeyer flask, in which he places 40 c.c. of glacial acetic acid and 15 g. of a mixture of equal parts of zinc dust and iron powder; 50 c.c. of nitrate solution, corresponding to 0.5 g. substance, are allowed then to flow in with constant shaking, and the shaking is repeated again vigorously at the end of the distillation. A brisk evolution of hydrogen begins immediately, and continues for about fifteen minutes; after the lapse of this period an equal quantity of the mixture of metals is added again and the mixture shaken round. Should the whole solidify to a pasty mass, about 30 c.c. of water must be added. The reduction is complete in thirty to forty minutes; sodium hydroxide is then added, and the ammonia distilled off.

Stutzer<sup>2</sup> converts the nitric acid into ammonia by the action of aluminium foil in alkaline solution. The reduction takes about twelve hours.

Devarda<sup>3</sup> has suggested the following method, based on the conversion of nitric acid into ammonia by the action of aluminium and zinc powder in dilute potassium hydroxide solution. One-half gram of substance is placed in a flask and treated with about 60 c.c. of water, 5 c.c. of alcohol, and 50 c.c. of potassium hydroxide of sp. gr. 1.3; 2 to 2.5 g. of an alloy are then added, consisting of forty-five parts of aluminium, fifty parts of copper, and five parts of zinc. After connect-

<sup>1</sup> *Chem. Zeit.*, 1890, 14, i., 410.

<sup>2</sup> *Z. angew. Chem.*, 1890, 3, 695.

<sup>3</sup> *Landw. Versuchs-Stat.*, 1893, 42, 130.



ing the flask to the distillation apparatus, the former is gently warmed and the whole is left to stand for half an hour; the reaction is then practically complete and the ammonia can be distilled off.

This method cannot be applied when nitrogenous organic substances are present.

Other methods have been described by W. Ackermann<sup>1</sup> and by Bohlig.<sup>2</sup>

**5. Estimation by means of the Nitrometer.**—This method is fully described in Vol. I., p. 315.

**Note.**—The “Fertilisers and Feeding Stuffs (Methods of Analysis) Regulations 1908,” which had been framed by a Committee appointed by the Board of Agriculture and Fisheries in pursuance of the provisions of the Fertilisers and Feeding Stuffs Act, 1906, has now received parliamentary sanction. As most of the determinations of nitrogen and of the other constituents of fertilisers are required for the valuation of the materials used in the manufacture of fertilisers, or in the testing of the fertilisers as supplied to farmers, the processes prescribed by the Board of Agriculture and Fisheries must now be regarded as official. Whatever the merits of other processes hitherto used may have been, the sanction by the Government of the prescribed processes practically renders impossible their further use, as in all official matters the only methods which would be recognised here are those which have been carried out according to the instructions given in the “Fertilisers and Feeding Stuffs (Methods of Analysis) Regulations, 1908.”

Under these circumstances it is practically useless to discuss the merits or demerits of other processes so far as English practice is concerned, and so far as the desired estimations come within the scope of the prescribed Regulations.

The directions given in the Regulations simply lay down the processes which must be followed, but do not enter into details of the apparatus to be used, or in some cases the quantities to be employed. The descriptions given in the text will, however, enable any qualified analyst to comply with the Regulations, and with due care the processes detailed are capable of yielding very accurate results.

For the sake of reference the Regulations are reproduced at the end of the article on “Feeding Stuffs,” on p. 469 of this volume. (Smetham).

## 2. ESTIMATION OF PHOSPHORIC ACID

Phosphoric acid occurs in artificial manures in four different forms. In some manures it may only be necessary to estimate one form; in others two forms, and in some cases even three forms must be determined.

<sup>1</sup> *Chem. Zeit.*, 1898, 21, 690.

<sup>2</sup> *Z. anal. Chem.*, 1898, 37, 498.

It was formerly supposed that, since phosphoric acid is a tribasic acid of the composition  $\text{H}_3\text{PO}_4$ , it would give rise to only three series of salts :—

$\text{CaH}_4(\text{PO}_4)_2$  monobasic calcium phosphate.

$\text{Ca}_2\text{H}_2(\text{PO}_4)_2$  dibasic calcium phosphate.

$\text{Ca}_3(\text{PO}_4)_2$  tribasic calcium phosphate.

Hilgenstock and Stutzer<sup>1</sup> found that the phosphoric acid in basic slag is present in the form of a tetrabasic calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2\text{CaO}$ ).

Monobasic calcium phosphate is soluble in water; the phosphoric acid present in manures in the form of this salt and as free phosphoric acid is designated and estimated as "Phosphoric acid soluble in water."

In the United Kingdom, according to the general trade custom, and by the Fertilisers and Feeding Stuffs Act, 1906, "Soluble Phosphate" is held to mean the amount of tribasic calcium phosphate which has been rendered soluble in water; or, in other words, the amount of phosphoric acid soluble in water, stated in terms of tribasic calcium phosphate.

Dibasic phosphates, even if not originally present in manures, may be formed by double decomposition between iron and aluminium compounds on the one hand, and monobasic calcium phosphate on the other. This change is known as the "Reversion" of phosphoric acid, and, in the analysis, either dibasic calcium phosphate, or else reverted (retrograde) phosphoric acid is estimated. Dibasic calcium phosphate is insoluble in water, but dissolves in ammonium citrate solution.

Tribasic phosphates of calcium, aluminium, and iron are insoluble in water. They occur in natural phosphates (phosphorite, apatite, bone meal, etc.), and are dissolved by strong acids.

Tetrabasic calcium phosphate is only found in basic slag, and it is to this peculiar combination that the rapid action of basic slag is attributable. Dilute ammonium citrate solution and dilute citric acid dissolve nearly all the phosphoric acid combined in this form as readily as they dissolve precipitated or dibasic calcium phosphate. It was at first difficult to explain why the phosphoric acid of basic slag, which was supposed to be combined as tribasic calcium phosphate, should be considerably more efficient in its action than is the phosphoric acid of phosphorite, etc.; this abnormal property is now explained by the form in which the phosphoric acid in basic slag is combined with the calcium.

The value of phosphates decomposed by sulphuric acid is generally gauged by the percentage of phosphoric acid soluble in water; in the case of other manures, such as precipitated phosphate of lime, dibasic calcium phosphate soluble in ammonium citrate solution is estimated; in other cases, such as phosphorite, tribasic phosphate is determined,

<sup>1</sup> *Repertorium der analytischen Chemie*, 1886, 6, 425.

while in basic slag, tetrabasic phosphate, or the phosphoric acid soluble in citric acid solution is estimated. Superphosphates which have not been completely decomposed, or which contain iron and alumina, as well as other incompletely decomposed manures, contain phosphoric acid in all three forms, viz., soluble in water, soluble in citrate solution, and insoluble.

Special analytical methods must accordingly be adopted for the estimation of the different forms of phosphoric acid.

#### A. VOLUMETRIC ESTIMATION OF INSOLUBLE OR TOTAL PHOSPHORIC ACID

The volumetric estimation of insoluble phosphoric acid is antiquated and the method is not accurate. In all cases, however, in which phosphates with a very low percentage of ferric oxide and alumina are to be examined, this method gives results which are often sufficiently accurate for use in works; it is accordingly still used in some cases for commercial analysis, especially on account of its rapidity.

The method is carried out as follows:—Five grams of the substance to be examined are completely incinerated in a platinum dish, and then dissolved in moderately strong hydrochloric acid. The solution is transferred to a 250 c.c. flask, made up to the mark, and 50 c.c. of this solution treated with a slight excess of ammonia in an Erlenmeyer flask; the precipitate formed is redissolved by addition of acetic acid. Ten c.c. of ammonium acetate solution (100 g. ammonium acetate and 100 g. of concentrated acetic acid per litre) are added, and the process continued as described under the following head (B).

#### B. VOLUMETRIC ESTIMATION OF PHOSPHORIC ACID SOLUBLE IN WATER

The volumetric estimation of phosphoric acid in superphosphates, etc., is only permissible in the case of samples not containing more than 1 per cent. of phosphoric acid combined with iron and alumina.

If the manure does not contain much more than 20 per cent. of phosphoric acid, 200 c.c. of the aqueous solution of the sample (20 g. : 1000 c.c. of water) are treated with 50 c.c. of ammonium acetate solution (see above), in order to precipitate, if necessary, the phosphates of iron and alumina. After standing for two hours, any precipitate which may have been formed is filtered off, washed three times with hot water, ignited and weighed; half its weight is reckoned as phosphoric acid ( $P_2O_5$ ). In the case of phosphates containing much more than 20 per cent. of phosphoric acid soluble in water, 100 c.c. of the filtered solution are diluted with 100 c.c. of distilled water,



50 c.c. of ammonium acetate added, and the process continued as above.

The titration is carried out as follows:—Fifty c.c. of the filtrate from the ferric phosphate (which of course must not be diluted by the washings from the latter) are placed in an Erlenmeyer flask; these 50 c.c. will contain 40 c.c. of the original solution and 10 c.c. of ammonium acetate solution. Standard uranium solution is then run in from a burette until a drop of the liquid forms a brown ring when brought into contact with a drop of freshly prepared potassium ferrocyanide solution; the test is performed by dipping a glass rod into the liquid, and spreading out the drop thus obtained on a white porcelain plate; a drop of the ferrocyanide solution is allowed to drop on to this. The liquid must be boiled up after each addition of uranium solution; the boiling, however, always causes some calcium phosphate to be carried down by the uranium precipitate, so that a preliminary titration must always be made. Then, in the second titration, that amount of uranium solution is run in, which, in the first titration, was required to produce a slight reaction; the solution is then heated to boiling, and tested with potassium ferrocyanide. If no reaction is observed, a further 0.2 c.c. of uranium solution are added, the solution boiled, and again tested with potassium ferrocyanide. This operation is repeated until the colour reaction obtained exactly corresponds to that originally taken as the end-point, in standardising the uranium solution. The final result should always be checked by several titrations.<sup>1</sup>

Titration with uranium is advisable only in the case of phosphates free from iron and alumina; if these are present, the phosphoric acid is estimated almost as rapidly and with greater certainty by the gravimetric citrate method.

<sup>1</sup> To prepare the standard uranium solution (1 c.c. = 0.005 g.  $P_2O_5$ ), 1000 g. of pure uranium nitrate are dissolved in 28,200 c.c. of water, and the small quantity of free nitric acid, which is generally present, neutralised by adding 100 g. of ammonium acetate. This solution is left to stand for several days, and is then filtered from the sediment. It is standardised either by means of a solution of a superphosphate, which contains 16 per cent. of phosphoric acid, soluble in water, and is completely free from iron, or by a solution of pure tricalcium phosphate. The latter is prepared by digesting 5.5 g. of dry tricalcium phosphate with dilute sulphuric acid; the acid should contain 2.85 to 2.9 g.  $SO_3$  to 5.5 g. of the salt; after digestion, the mass is dissolved in water, made up to a litre, and filtered, after standing for some time, from the separated calcium sulphate, and any phosphate which may not have been acted on. The phosphoric acid in 50 c.c. of this solution is then estimated gravimetrically. As an alternative to this method, 5.5 g. of pure tricalcium phosphate may be dissolved in the least possible quantity of nitric acid, the solution made up to a litre, and the phosphoric acid determined in 50 c.c. The mean of four or six closely concordant readings are taken as the titre of the solution. The solution must always be tested for pyrophosphoric acid. The uranium solution is diluted till 1 c.c. = 0.005 g.  $P_2O_5$ . The standardised solution must be carefully stoppered, and stored in a dark place, and must be re-standardised from time to time.

C. GRAVIMETRIC ESTIMATION OF INSOLUBLE AND  
TOTAL PHOSPHORIC ACID

**1. Molybdate Method.**—This method was formerly regarded as the most reliable gravimetric method of estimating phosphoric acid, and was, therefore, always exclusively used in cases of arbitration. Of late years, however, it has been superseded by the more simple citrate method.<sup>1</sup> The molybdate method has been worked out by a number of chemists, so that various special directions have been recommended. Of the numerous modifications that have been proposed, two only will be described in detail; these, however, have been thoroughly tested, are easy of execution, and give absolutely certain results.

**1. Wagner's Method.**—Twenty-five or 50 c.c. of the phosphate solution, free from silica, containing 0.1 to 0.2 g.  $P_2O_5$ , are placed in a beaker, and concentrated ammonium nitrate solution and molybdate solution added until the total liquid contains 15 per cent. of ammonium nitrate, and not less than 50 c.c. of molybdate solution to every 0.1 g.  $P_2O_5$ .

The addition of ammonium nitrate effects a saving in molybdate solution; in presence of 15 per cent. ammonium nitrate about half as much molybdate suffices for precipitation as would otherwise be necessary; the above conditions also effect more rapid and complete separation of the molybdate precipitate.

The contents of the beaker are heated on the water-bath to 80° to 90°, kept at this temperature for ten minutes, and then placed aside and left to stand for about an hour; the liquid is then filtered, and the precipitate washed with dilute ammonium nitrate solution until the filtrate is free from calcium. Accurate results are obtained when acidified ammonium nitrate solution is used for washing, since P. Wagner's experiments have shown that 100 c.c. molybdate solution, or 100 c.c. ammonium nitrate solution, dissolve less than 0.1 mg.  $P_2O_5$ . The beaker is then placed beneath the funnel, the filter pierced by a platinum wire, and the precipitate washed into the beaker by means of 2.5 per cent. ammonia solution, the filter being washed perfectly clean; the precipitate is stirred round till dissolved, and more 2.5 per cent. ammonia added until the total volume of the liquid amounts to about 75 c.c. Magnesia mixture (10 c.c. to every 0.1 g.  $P_2O_5$ ) is then added, drop by drop, (the magnesia mixture must in all cases be added gradually, or drop by drop, even when the ammoniacal solution of the molybdate precipitate has previously been approximately neutralised by hydrochloric acid) and with constant stirring, the beaker covered with a glass plate, and left to stand for two hours. The precipitate is filtered off, washed with 2.5 per cent. ammonia until the filtrate is free

<sup>1</sup> Cf. *Fertilisers and Feeding Stuffs (Methods of Analysis) Regulations*, p. 473.

from chloride, and dried. The dried precipitate and rolled-up filter are then transferred to a weighed platinum crucible, the lid adjusted, and the filter charred; the crucible, placed in an inclined position, is finally ignited for ten minutes over a good Bunsen burner, then for five minutes on the blowpipe, and allowed to cool in a desiccator, and weighed.

*Composition of the Reagents.*

1. *Molybdate Solution*.—One hundred and fifty grams of ammonium molybdate are dissolved in water, diluted to 1 litre with water, and poured into 1 litre of nitric acid of sp. gr. 1.2.

2. *Concentrated Ammonium Nitrate Solution*.—Seven hundred and fifty grams of ammonium nitrate are dissolved in water and diluted to 1 litre.

3. *Dilute Ammonium Nitrate Solution for Washing*.—One hundred and fifty grams of ammonium nitrate and 10 c.c. of nitric acid are dissolved in water and made up to 1 litre.

4. *Magnesia Mixture*.—Fifty-five grams of crystallised magnesium chloride and 70 g. of ammonium chloride are dissolved in 1 litre of 2½ per cent. ammonia.

Märcker adds molybdate solution, and warms for three hours at 50°, then thoroughly washes the yellow precipitate with dilute molybdate solution (1 : 1), and dissolves from the filter with 5 per cent. ammonia; the filter is not pierced in this case. The solution is finally neutralised with hydrochloric acid and precipitated with a magnesia mixture containing a larger quantity of ammonia and ammonium chloride (550 g. magnesium chloride, 1050 g. ammonium chloride, 3.5 litres 24 per cent. ammonia, and 6.5 litres distilled water).

Fresenius adds molybdate solution, and warms for four to six hours at 50°; the precipitate is washed with a solution obtained by mixing one hundred parts of molybdate solution, twenty parts of nitric acid of sp. gr. 1.2, and eighty parts of water. The yellow precipitate is then dissolved in ammonia (which must be as dilute as possible), the solution approximately neutralised, 6 to 8 c.c. of ammonia of sp. gr. 0.925 added, the solution precipitated with magnesia mixture, and then a further 20 c.c. of ammonia added.

2. *Böttcher's Method*.—The following form of the molybdate method has been used for some years in the laboratories in Möckern, and is to be highly recommended:—

The phosphate is dissolved in nitric acid; if hydrochloric acid be used as the solvent, the solutions must be evaporated to dryness, taken up with nitric acid, filtered, and the filtrate precipitated with molybdate solution. Twenty-five or 50 c.c. of the solution, containing 0.1 to, at the most, 0.2 g. of phosphoric acid, and which



must be free from silica, are placed in a beaker or Erlenmeyer flask of about 300 c.c. capacity, molybdate solution added (about 100 c.c. to every 0.1 g. phosphoric acid), and the whole digested for four to six hours on the water-bath at 60°. When cold, a small sample of the supernatant liquid is filtered into a test tube, double its volume of molybdate solution added, and boiled up; if any further precipitate is formed the liquid must be returned to the beaker or flask, a corresponding further quantity of molybdate solution added, and the contents again digested for some time. If the filtrate, on the other hand, remains clear when warmed with molybdate solution, or if only a white precipitate of molybdic acid separates, the total liquid is filtered when cold, and the yellow precipitate repeatedly washed by decantation (eight or nine times) with dilute molybdate solution (1:3) or with dilute ammonium nitrate solution (*cf.* p. 390). Dilute nitric acid (1 per cent.) may also be used for washing, or as an alternative, a solution made up by mixing one hundred parts of molybdate solution, twenty parts of nitric acid of sp. gr. 1.2, and eighty parts of water. The washing must be continued until the filtrate is free from calcium, which is tested for by adding an excess of ammonia and then ammonium oxalate to a portion of the filtrate; or 1 c.c. of the washings may be treated with 10 c.c. of absolute alcohol which has been acidified with a little sulphuric acid; in either case no turbidity should be produced. The filtration and washing must of course be carried out in an atmosphere free from ammonia. The yellow precipitate of ammonium phospho-molybdate is dissolved in warm, dilute ammonia (1:3), the solution filtered through the original filter, and the beaker or flask, as well as the filter, completely washed with hot water to which a few drops of ammonia have been added. The filtrate is treated with concentrated hydrochloric acid until the yellow precipitate first formed no longer redissolves immediately but goes into solution very gradually. When the mixture is again quite cold, magnesium chloride mixture (10 c.c. to every 0.1 g.  $P_2O_5$ ) is added, drop by drop, the liquid being continually stirred with a glass rod without touching the sides of the beaker; concentrated ammonia is added to the extent of one-third of the volume of the liquid, bringing the total volume up to about 110 c.c., the mixture stirred round, and then left to stand for two hours in a cool place. The liquid is then filtered, the precipitate of magnesium ammonium phosphate transferred to the filter and washed with dilute ammonia (1:3) until the filtrate no longer gives any chloride reaction. The filter and precipitate are then either transferred to a weighed platinum crucible and the former burnt wet, or they are dried first, the precipitate transferred to the crucible, and the filter paper incinerated on a platinum wire; the ash is then added to the precipitate and moistened with two or three

drops of nitric acid. The platinum crucible is first very gently warmed to avoid spirting, then heated more strongly, and finally ignited for ten minutes in a very good Bunsen flame, or for five minutes on the blow-pipe or in a Rössler furnace, when a white residue should be obtained. The crucible is then allowed to cool in a desiccator, and weighed, and the ignition repeated until the weight is constant. After igniting and weighing, a drop of neutral silver nitrate solution is placed on the precipitate, when no yellow coloration should be formed. The weight of magnesium pyrophosphate (after subtraction of that of the filter ash), multiplied by 0.6379, gives the amount of phosphoric acid contained in 25 or 50 c.c. respectively of the phosphate solution.

It is not advisable to filter the precipitate through a perforated Gooch crucible fitted with asbestos, as finely crystalline precipitates very easily pass through this form of filter, and the filtration has then to be repeated.

*Composition of the Reagents.*

1. *Molybdate Solution*.—Five hundred grams of pure molybdic acid are dissolved in a mixture of 1 litre of water and 1 litre of ammonia (sp. gr. = 0.91), and this solution gradually poured into 8 litres of dilute nitric acid, made by mixing 2 litres of nitric acid of sp. gr. 1.4 with 6 litres of water.

2. *Magnesia Mixture*.—Five hundred grams of crystallised magnesium chloride and 700 g. of ammonium chloride are dissolved in water, 3500 c.c. of ammonia of sp. gr. 0.97 added, and the solution diluted to 10 litres.

H. Neubauer<sup>1</sup> has proved that when magnesium pyrophosphate is strongly ignited at a high temperature, loss is incurred owing to volatilisation of phosphoric acid; the latter is retained by magnesia placed on the lid of the platinum crucible, and can be qualitatively identified in the magnesia; it was, therefore, proposed to apply a corresponding correction to the results of phosphoric acid estimations by the molybdate method. As the result of investigations on the estimation of phosphoric acid by the different modifications of the molybdate method carried out by the Union of Agricultural Laboratories in Germany, it has, however, been proved that it would be quite erroneous to apply Neubauer's correction data to all estimations by the molybdate method. The application of these results is only justified when Neubauer's method is followed. This method consists in precipitation from a solution containing 2½ per cent. of ammonia. On the other hand, when the precipitation with magnesia mixture takes place after exact or approximate neutralisation, as is customary in the majority of laboratories, correct results are obtained directly, and the

<sup>1</sup> Inaugural Dissertation, Rostock, 1893.

application of Neubauer's correction would then render the results too high.<sup>1</sup>

**2. Citrate Method.**—This is a so-called compensation method; the estimations agree, however, not only amongst themselves, but are also in extremely close agreement with those of the molybdate method.

The phosphoric acid is precipitated directly by magnesia mixture, the simultaneous precipitation of calcium, iron, alumina, etc., being prevented by previous addition of ammonium citrate. A fraction of the bases is, however, always carried down; on the other hand, a corresponding fraction of phosphoric acid escapes precipitation, so that the one completely compensates for the other, and thoroughly reliable results are obtained.

In the case of aqueous solutions of superphosphates, 50 c.c. of solution (= 1 g. substance) are treated with 50 c.c. of citrate solution, prepared according to the directions given below.

The addition of the citrate solution must not render the liquid permanently turbid; the precipitate which generally forms must disappear again on stirring. If this is not the case, more citrate solution must be added, until the precipitate redissolves. Solutions prepared from bone-black superphosphates sometimes appear opalescent after addition of citrate solution; this, however, does not influence the results. When acid solutions of basic slag, bone-meal, etc., are treated with citrate solution, heat is evolved; the solution must, therefore, be cooled before precipitation with magnesia mixture. When bone-meal, fish guano, basic slag, etc., have been dissolved in aqua regia or in sulphuric acid, 50 c.c. of the solution (= 0.5 g. substance) are treated with 100 c.c. of the same citrate solution. If magnesia mixture be added a long time after the addition of the citrate solution, calcium phosphate is apt to separate in a crystalline form.

In every case 25 c.c. of magnesia mixture are then immediately added; to accelerate precipitation the mixture should either be shaken for half an hour in a shaking apparatus, or stirred for half an hour by a mechanical stirrer; it is then filtered. According to Halenke, complete precipitation of the phosphoric acid after ten minutes' standing may also be effected by drawing a glass rod, covered with rubber, twice round the inner wall of the beaker. Filtration is most rapidly carried out in a platinum Gooch crucible fitted with a layer of fine asbestos, and may be done either immediately after shaking or stirring, or after the liquid has stood for some time. The magnesium ammonium phosphate is washed into the crucible by means of a 5 per cent. ammonia solution, and the precipitate washed by filling up the crucible five or six times successively with 5 per cent. ammonia. The outside of the crucible is dried by placing it on filter paper, then further

<sup>1</sup> Cf. *Landw. Versuchs-Stat.*, 1895, 45, 365.



dried by standing it on a heated iron or porcelain plate until the precipitate begins to crack, ignited for three to five minutes in a Rössler furnace, allowed to cool in a desiccator, and weighed. The crucible may then be used again for the filtration of another precipitate; from thirty to forty estimations may be carried out consecutively without renewing the asbestos.

Asbestos for filtration purposes is prepared as follows:—Best quality, long-fibre asbestos is placed on a glass plate and cut with a knife into fine shavings. About 10 g. of the shavings are extracted with boiling, concentrated hydrochloric acid for two hours, the acid then poured off through a wire gauze, and the last traces of acid as well as the very fine asbestos fibres removed by repeatedly washing the asbestos by decantation with distilled water in a large beaker. The remaining asbestos is suspended in water, transferred to a litre bottle, and is then ready for use. Each filter requires about 20 c.c. of liquid, which is poured into the crucible after thoroughly shaking up. The asbestos is washed several times in the crucible with distilled water with the aid of the pump; it must be pressed down with a glass pestle, so that it is uniformly distributed over the bottom of the crucible, particular care being taken to make it fit well on to the edges of the crucible. The latter is ignited for ten minutes in a Rössler furnace, weighed when cold, and is then ready for use.

#### *Composition of the Reagents.*

1. *Citrate Solution*.—Eleven hundred grams of purest citric acid are dissolved in water, the solution treated with 4000 c.c. of 24 per cent. ammonia, and then diluted to 10,000 c.c.

2. *Magnesia Mixture*.—Five hundred and fifty grams of magnesium chloride and 1050 g. ammonium chloride are dissolved in a mixture of 6500 c.c. of water and 3500 c.c. of 24 per cent. ammonia.

3. **Other Methods**.—E. A. Grete<sup>1</sup> recommends the estimation of phosphoric acid by titration with molybdate solution and gelatine.

P. Neumann<sup>2</sup> recommends Hanamann's method of estimation as phospho-molybdic anhydride.

R. Striegler<sup>3</sup> has proposed a method for the estimation of phosphoric acid by means of the refractometer.

These methods have rarely, if ever, been applied, since they are not more convenient than the simple and reliable citrate method.

4. **Estimation of Phosphoric Acid as Phospho-molybdic Anhydride**.—When a nitric acid solution of phosphate is precipitated in presence of ammonium nitrate, a compound of phosphoric and molybdic acids is obtained which, on ignition in a definite manner,

<sup>1</sup> *Ber.*, 1888, 21, 2762; 1909, 42, 3106.

<sup>2</sup> *Z. anal. Chem.*, 1898, 37, 303.

<sup>3</sup> *Bull. Soc. Sci. diu Buc.*, 1898, 7, 172.

is transformed into a well-characterised anhydride of constant composition possessing the formula  $24\text{MoO}_3 \cdot \text{P}_2\text{O}_5$ . Woy<sup>1</sup> recommends that the estimation of phosphoric acid be effected by weighing this compound.

*Composition of the Reagents.*

1. *Ammonium Molybdate Solution.*—Three per cent. aqueous solution of ammonium molybdate, prepared by dissolving 120 g. of best commercial ammonium molybdate in distilled water, making up to 4 litres, and filtering if necessary.

2. *Ammonium Nitrate Solution.*—Three hundred and forty grams of ammonium nitrate to 1 litre of water.

3. *Nitric Acid*, of sp. gr. 1.153, containing 25 per cent.  $\text{HNO}_3$ .

4. *Solution for Washing*, containing 5 per cent. of ammonium nitrate and 1 per cent. of nitric acid. Two hundred grams of ammonium nitrate and 160 c.c. of nitric acid made up to 4 litres.

*Principle of the Precipitation.*—One-tenth gram  $\text{P}_2\text{O}_5$  requires 2.9856 g. ammonium molybdate, = 100 c.c. of a 3 per cent. solution, in order to form the anhydride  $24\text{MoO}_3 \cdot \text{P}_2\text{O}_5$ . One milligram of phosphoric acid to be precipitated requires 1 c.c. of solution, hence 0.5 g. of substance are used and 5 c.c. of molybdate solution are taken for every 1 per cent. of phosphoric acid. An excess of 20 c.c. over and above the amount of solution theoretically necessary for precipitation is ample. For 0.1 g. of phosphoric acid 1.16 g. of nitric acid are required; nitric acid up to 3.56 g. is not liable to cause dissociation. Since a certain amount of nitric acid is used up in decomposing the ammonium molybdate, and also, perhaps, in secondary reactions, 10 c.c. of nitric acid are taken, and in particular cases this amount may be increased to 20 c.c.; there is always an excess of at least 20 c.c. of molybdate solution (= 0.6 g. molybdate) present, and this prevents dissociation and suffices to counteract the effect of an excess of 30 g. of nitric acid.

Ammonium nitrate must be present to the extent of about 5 per cent. The total volume of liquid generally amounts to approximately 200 c.c.; hence, 30 c.c. of ammonium nitrate solution must be taken.

*The Precipitation.*—The measured volume of phosphate solution is placed in a 400 c.c. beaker, 30 c.c. of ammonium nitrate solution, and either 10 or 20 c.c. of nitric acid measured out together in the same measuring glass, added, and the mixture heated to boiling over a gauze. The required amount of molybdate solution is also heated to boiling, transferred to a stopcock funnel, and allowed to run in, drop by drop, into the middle of the hot phosphate solution, which must be continually shaken round during the addition. The beaker is then stirred for another minute, and placed aside; the liquid may be filtered

<sup>1</sup> *Chem. Zeit.*, 1897, 21, 441; 1903, 27, 279.

in ten to fifteen minutes. Porcelain Gooch crucibles are used for the filtration, which are prepared as follows:—The asbestos (*cf.* p. 394) is broken up as finely as possible by shaking it with water in a small Erlenmeyer flask, and the Gooch crucible filled with a sufficient quantity to give a thin uniform layer on applying the pump; the layer need only be very thin, owing to the ease with which the phospho-molybdate precipitate filters. A perforated porcelain plate, such as are supplied with porcelain Gooch crucibles, is placed in the crucible, the latter filled two or three times with water, the perforated plate removed and the crucible dried over a burner, and finally ignited for a short time in a platinum crucible.

The supernatant liquid of the phospho-molybdate precipitate is then decanted through the weighed Gooch crucible with the help of the pump; the precipitate is next stirred up with about 50 c.c. of the washing solution (No. 4) previously heated, thoroughly agitated several times, and allowed to settle again. After five minutes the supernatant liquid is again filtered off and the precipitate dissolved in 10 c.c. of 8 per cent. ammonia. Twenty c.c. of ammonium nitrate solution, 30 c.c. of water, and 1 c.c. of molybdate solution are then added, the solution boiled and precipitated with 20 c.c. of hot nitric acid. After standing for ten minutes this is filtered through the crucible first used, the precipitate washed once with washing solution and twice with alcohol. The Gooch crucible is then placed in a nickel crucible (4.5 cm. high and 5 cm. in diameter at the top), a perforated porcelain plate being placed at the bottom of the nickel crucible; the latter is first heated with a small flame, and the temperature then gradually raised till the crucible attains a low red-heat. The original yellow precipitate is thus converted into the black anhydride in about fifteen minutes; the conversion is complete when the surface of the precipitate, after passing through various colorations, changes from a lustreless velvety to a lustrous crystalline appearance and is of a uniform dark blue-black colour. In this form the composition remains perfectly constant, even when subjected to further moderate ignition. Too strong ignition is easily detected by local lighter coloured, whitish appearances on the surface; the precipitate has the composition  $24\text{MoO}_3 \cdot \text{P}_2\text{O}_5$ , and contains 3.946 per cent.  $\text{P}_2\text{O}_5$ .

The following quantities are employed for the various manures:—

(a) *Superphosphates*.—Twenty-five c.c. of an aqueous solution (20 g.: 1 litre) + 10 c.c. of nitric acid + 30 c.c. of ammonium nitrate are heated to boiling, and precipitated by 100 c.c. of 3 per cent. boiling molybdate solution; the precipitate is washed once by decantation, using 50 c.c. of washing solution, and then dissolved in 10 c.c. of ammonia; to this solution are added 20 c.c. of ammonia nitrate, 30 c.c. of water, and 1 c.c. of molybdate solution. The precipitation is



effected by boiling with 20 c.c. of nitric acid, and the precipitate filtered off after fifteen minutes.

(b) *Basic Slag*.—1. *Total Phosphoric Acid*.—Fifty c.c. of the sulphuric acid solution of the substance (5 g.: 500 c.c.) are nearly neutralised by 24 per cent. ammonia, 20 c.c. of nitric acid and 30 c.c. of ammonium nitrate added, and the boiling solution precipitated by 120 c.c. of 3 per cent. boiling molybdate solution; 2. *Phosphoric Acid soluble in Citric Acid*.—Fifty c.c. of the citric acid solution (5 g.: 500 c.c.) are treated with 30 c.c. of nitric acid of sp. gr. 1.153 (25 per cent.) and 45 c.c. of ammonium nitrate, the solution heated to boiling, and precipitated by 100 c.c. of 6 per cent. boiling molybdate solution.

(c) *Bone-Meal*.—Fifty c.c. of the acid solution (5 g.: 500 c.c.) are nearly neutralised with 24 per cent. ammonia, 30 c.c. of ammonium nitrate and 20 c.c. of nitric acid added, the mixture heated to boiling, and precipitated by 150 c.c. of 3 per cent. boiling molybdate solution.

### 5. Lorenz's Method.<sup>1</sup>

#### *Composition of the Reagents.*

1. *Sulphate-Molybdic Acid Reagent*.—One hundred grams of pure, dry ammonium sulphate are dissolved in 1 litre of nitric acid of sp. gr. 1.36 at 15° in a 2 litre flask; 300 g. of dry, pure ammonium molybdate are dissolved in hot water in a litre flask, the solution cooled to about 20°, made up to the mark, and then poured, in a thin stream, with constant stirring, into the above nitric acid solution. The whole is then allowed to stand for forty-eight hours at the ordinary temperature, and filtered through a dense, acid-resisting filter paper. The solution is kept in well-stoppered bottles in a cool place and in the dark.

2. *Nitric Acid* of sp. gr. 1.20 at 15°.

3. *Nitric Acid in Sulphuric Acid Solution*.—Thirty c.c. of sulphuric acid of sp. gr. 1.84 are added to 1 litre of nitric acid of sp. gr. 1.20 at 15°. Nitric acid of this specific gravity (1.20) is prepared by mixing 357 c.c. of nitric acid of sp. gr. 1.411 with 500 c.c. of water.

4. *Ammonium Nitrate*.—A 2 per cent. aqueous solution is used; if it is not acid it is acidified with a few drops of pure nitric acid per litre.

5. *Alcohol*.—Alcohol of 90 to 95 per cent. by volume, which should leave no residue on evaporation and must not give an alkaline reaction.

6. *Ether*.—This should leave no residue on evaporation, not give an alkaline reaction, be free from alcohol, and not contain too much water; 150 c.c. should be miscible with 1 c.c. of water to a homogeneous solution at 15°.

<sup>1</sup> *Landw. Versuchs-Stat.*, 1901, 55, 183.

*Preparation of Samples for Analysis.*

1. *Phosphoric Acid soluble in Water.*—In the case of superphosphate, potassium superphosphate, etc., 20 g. are dissolved in 1 litre of water in the usual way. For the estimation of phosphoric acid by the ether drying method (cf. *infra*), 10 c.c. of the superphosphate solution, = 0.2 g. substance, are taken. In the case of double superphosphates, 10 g. are dissolved in 1 litre of water and 10 c.c. taken for the estimation of phosphoric acid by the ether method. With superphosphate, precipitated phosphates, etc., the extract is prepared by Petermann's method in the usual way, and 10 c.c. of the solution are taken for the ether method of estimation.

2. *Phosphoric Acid soluble in Citric Acid, Basic Slag, etc.*—A solution in 2 per cent. citric acid is prepared according to Wagner's method (p. 405); for the ether method estimation, 15 c.c. of the solution, = 0.15 g. substance, are taken.

3. *Total Phosphoric Acid:*—

(a) *Superphosphate, Basic Slag.*—Five grams of the sample are treated with 35 c.c. of concentrated sulphuric acid, either with or without the addition of a little nitric acid. As an alternative method, 5 g. are dissolved in 100 c.c. of nitric acid and the solution made up to 500 c.c.; 15 c.c., = 0.15 g. of substance, are taken for the estimation by the ether method.

(b) *Bone-meal, Mineral Phosphates, Precipitated Phosphates, Double Superphosphates, Guano*, and all other manures not specifically referred to elsewhere which contain more than 10 per cent. of phosphoric acid. Five grams are dissolved in 50 c.c. of concentrated sulphuric acid, either with or without the addition of nitric acid. An alternative method is to dissolve 5 g. in 100 c.c. of nitric acid and make up the solution to 500 c.c.; 10 c.c., = 0.1 g. of substance, are taken for the estimation by the ether method.

(c) *Horn-meal and other Artificial Manures*, which contain less than 10 per cent. of phosphoric acid. Ten grams are dissolved in 50 c.c. of concentrated sulphuric acid, or, to avoid the formation of dark coloured solutions, in 50 c.c. of concentrated sulphuric acid and a little nitric acid, or in 100 c.c. of nitric acid, and the solution diluted to 500 c.c. For the ether method estimation, 15 c.c. of the solution, = 0.3 g. substance, are taken.

(d) *Soils, etc.*, containing less than 1 per cent. of phosphoric acid. Twenty-five grams of the sample are dissolved in not more than 200 c.c. of nitric acid of any of the above concentrations in a 500 c.c. flask, 200 c.c. of water added, the solution cooled, 10 c.c. of concentrated sulphuric acid or a corresponding quantity of dilute acid added, and the whole made up to the mark. Fifty c.c. of this solution, = 2.5 g. substance, are

taken for the ether method estimation; this method can, of course, be applied also to the estimation of phosphoric acid in plant ashes, etc.

*The Gravimetric Estimation of Phosphoric Acid in Solutions of Artificial Manures, Soils, etc., as Phospho-molybdate by the Ether drying Method.*—The volume of the phosphoric acid solution to be taken for this estimation as described above (10, 15, 20, or 50 c.c.) is transferred to a 200 to 250 c.c. beaker by means of an accurate pipette. If the sample has been dissolved in sulphuric acid only, this volume is made up to 50 c.c. by the addition of nitric acid of sp. gr. 1.2 (Reagent No. 2). In all other cases the measured volume of solution is made up to 50 c.c. by the addition of the requisite volume of nitric acid in sulphuric acid solution (Reagent No. 3). No addition is made in the case of soils, as the volume of solution to be taken for the determination is 50 c.c.

The total 50 c.c. of solution thus prepared are heated to incipient boiling and 50 c.c. of the sulphate-molybdic acid solution (Reagent No. 1) added; as soon as the bulk of the precipitate has separated, at most after five minutes, the whole is thoroughly stirred with a glass rod for half a minute. After standing for two to eighteen hours, the precipitate is filtered off through a platinum Gooch crucible; in the case of soils, and generally, if less than 3 mg. of phosphorous pentoxide are present, the precipitate must be allowed to stand for twelve to eighteen hours. The Gooch crucible is not packed with asbestos, but is fitted with a piece of good filter paper free from ash and fat, and cut so as just to cover the holes but not touch the sides of the crucible; the crucible and paper must be previously weighed. A fully glazed porcelain Gooch crucible can also be used. The crucible is fitted on to a filter flask attached to a pump in the usual way, the paper moistened with water after starting the suction, and the precipitate then filtered off. The beaker and precipitate are washed four times successively with the 2 per cent. ammonium nitrate solution, care being taken to completely remove any particles of the precipitate that adhere to the sides of the beaker. The crucible is then filled once completely and twice successively to one-half with alcohol, which is pumped off completely between each filling. The precipitate is next similarly washed three times with ether, care being taken not to prolong the washing unnecessarily, as otherwise the precipitate may become very finely divided on account of the rapid drying, and pass through the filter paper. The crucible is then removed, wiped dry outside, and dried in an exiccator, exhausted to about 100 to 200 mm., without calcium chloride or sulphuric acid, for thirty minutes, and weighed. The precipitate thus obtained contains 3.295 per cent.  $P_2O_5$ .

This method gives good results and does not occupy appreciably more time than direct precipitation with citrate solution and magnesium mixture.



The contained silica of the phosphoric acid solution does not influence the results. Böttcher has obtained satisfactory results with basic slags rich in silica. Further, it is immaterial for the estimation whether the extract of basic slag is freshly prepared or has been kept for several days. The method is accordingly to be especially recommended for the estimation of the phosphoric acid, soluble in citric acid, in basic slag.

#### D. ESTIMATION OF "PHOSPHORIC ACID SOLUBLE IN CITRATE SOLUTION," IN SUPERPHOSPHATES, ETC.

The estimation of reverted (retrograde) phosphoric acid in superphosphates, of assimilable phosphoric acid (or that soluble in citrate solution) in precipitated phosphates and partially decomposed bone-meal, etc., has been the subject of a great deal of investigation; a uniformly reliable method for the estimation of this form of phosphoric acid has, however, not yet been found.

The estimation is founded on the solubility of this form of phosphoric acid in an acid or neutral solution of ammonium citrate; phosphoric acid soluble in water is, of course, also soluble in this solution, so that it is included in the estimation. The following factors may materially influence the results:—The proportion of substance to citrate solution, duration of digestion, and temperature of experiment, nature of the citrate solution (depending on its method of preparation), the presence of various substances such as gypsum, the state of division, etc. More or less consistent results can only be obtained by accurately adhering to one and the same method.

Of the various methods that have been suggested for the estimation of phosphoric acid soluble in citrate solution, the following are selected:—

**1. Petermann's Method.**<sup>1</sup>—One gram of a superphosphate containing more than 20 per cent. phosphoric acid, 2 g. where the latter amounts to between 10 and 20 per cent., 4 g. of superphosphates containing less than 10 per cent. phosphoric acid and 4 g. of compound manures, are taken for the estimation. The substance is powdered dry in a porcelain mortar, then triturated with 20 to 25 c.c. of water, the liquid being decanted on to a filter, and the filtrate collected in a 250 c.c. flask; this trituration is repeated three times. The whole of the solid is then transferred to the filter, and thoroughly washed with water until the filtrate amounts to about 200 c.c.; if the filtrate is turbid, one drop of nitric acid is added. The filter and solid residue are then placed in a 250 c.c. flask, 100 c.c. of ammonium citrate solution added, and the flask allowed to stand for fifteen hours at the ordinary temperature, with occasional shaking. The mixture is then digested on

<sup>1</sup> *Publications of the "Station agronomique de l'Etat de Gembloux."*

the water-bath for one hour at  $40^{\circ}$ , filled up to the mark when cold, and filtered; 50 c.c. of the filtrate, and 50 c.c. of the aqueous solution first prepared are then taken and mixed, the mixture boiled for ten minutes with 10 c.c. of concentrated nitric acid, and the total phosphoric acid soluble in water, plus that soluble in citrate solution, determined in this solution either by the molybdate or citrate method.

The citrate solution is prepared as follows:—Five hundred grams of citric acid are dissolved in water, neutralised by ammonia, the solution cooled, diluted to a sp. gr. 1.09, and ammonia of sp. gr. 0.92 added to the extent of 50 c.c. of ammonia per 1 litre of solution; the specific gravity of the final solution is 1.082 to 1.083.

In the case of the estimation in precipitated phosphates, 1 g. of substance is triturated in a mortar with 100 c.c. of ammonium citrate solution; this is washed into a 250 c.c. flask and the method then proceeded with as above.

This method is very involved and tedious, and does not afford more accurate results than the earlier abbreviated method.

**2. Wagner's Method.**—Wagner<sup>1</sup> carried out a series of experiments, extending over a number of years, with various cultivated plants and different soils, using the following phosphates as fertilisers, viz.: extracted mineral superphosphate and extracted double superphosphate, pure bone ash superphosphate, bicalcium phosphate, tricalcium phosphate, and ground mineral phosphate, and thus determined the fertilising value of these phosphates compared with that of phosphoric acid soluble in water. He then attempted to find an analytical method for the examination of mineral superphosphates, the results of which should accord, as accurately as possible, with those of the fertilising experiments, and thus arrived at the following method, which he recommends as reliable:—

Five grams of mineral superphosphate are triturated with dilute acid citrate solution and transferred to a 500 c.c. flask. The mixture is diluted to the mark with dilute citrate solution, left to stand for about eighteen hours at  $13^{\circ}$  to  $18^{\circ}$ , frequently shaken, and then filtered. The phosphoric acid in the filtrate is estimated either by the molybdate method, or by direct precipitation with magnesia mixture. The latter method is carried out as follows:—One hundred c.c. of the filtrate are treated with 50 c.c. of a mixture made up of equal volumes of alkaline citrate solution and magnesia mixture. To accelerate the separation of the precipitate, the solution is stirred for a few minutes with a glass rod, the lower end of which is covered with a piece of rubber tubing; the walls of the beaker should be rubbed with the rubber during stirring. The mixture is allowed to stand for a few hours, or overnight, and the precipitate then further treated in the

<sup>1</sup> *Chem. Zeit.*, 1886, **10**, 1937; 1887, **11**, 905.

usual way. If it be desired to complete the analysis more rapidly, the separation of the precipitate may be effected in an hour with the help of a stirring- or shaking-machine. The necessary solutions are prepared as follows :—

1. *Concentrated Acid Citrate Solution*.—One hundred and fifty grams of citric acid are placed in a litre flask, dissolved in water, neutralised by ammonia, 10 g. of citric acid added to the neutral solution, and the whole then diluted to the litre.

2. *Dilute Acid Citrate Solution*.—One volume of the concentrated acid citrate solution is diluted with four times its volume of water.

3. *Alkaline Citrate Solution*.—Two hundred grams of citric acid are dissolved in 20 per cent. aqueous ammonia, so that the volume of the solution amounts to 1 litre.

4. *Magnesia Mixture*.—Seven hundred c.c. of 8 per cent. aqueous ammonia and 1300 c.c. of water are poured on to 110 g. of pure crystallised magnesium chloride and 140 g. of ammonium chloride, and the solution filtered after standing for several days.

This method may also be applied to estimating the value of commercial precipitated phosphates. The results quoted by Wagner as examples show that his method gives accurate results and that it permits of the agricultural valuation of mineral superphosphates, of double superphosphates prepared from mineral phosphate, and also of precipitated phosphates, being determined with sufficient accuracy.

Böttcher has estimated phosphoric acid soluble in citrate solution, or “available” phosphoric acid by Wagner’s method, in a variety of samples of partially decomposed or prepared bone ash<sup>1</sup> and precipitated phosphate, and found that the figures thus obtained from bone ash preparations agreed almost exactly with those given by the old Hallen’s method, using 2.5 g. of substance and digesting for an hour at 40°. In the case of precipitated phosphates, Wagner’s method yields throughout higher figures than are obtained by Petermann methods, but the former is to be preferred, as it rests on a scientific basis. It is accordingly advisable to estimate the phosphoric acid soluble in citrate solution, or “available” phosphoric acid, in all artificial manures, with the exception of basic slag, by Wagner’s method, particularly as this method still permits of simplification.

Böttcher has found that it is not necessary to allow the dilute acid citrate solution to act on the manures for eighteen hours; it suffices to treat the substance for thirty minutes with dilute citrate solution in a rotating shaking apparatus. Estimations of phosphoric acid, soluble in citrate solution, are thus carried out in a much shorter time, and results by different analysts are more likely to agree.

<sup>1</sup> *Chem. Zeit.*, 1898, 22, 21.



The estimation of phosphoric acid, soluble in citrate solution, in superphosphates, bone meal, precipitated phosphates, etc., is accordingly carried out as follows:—Five grams of substance are finely triturated with dilute acid citrate solution (No. 2), the mixture washed into a Stohmann 500 c.c. flask, filled up to the mark with dilute acid citrate solution at the ordinary temperature (about  $17^{\circ}5$ ), the flask closed with a rubber stopper, and placed in a rotating apparatus for thirty minutes; the apparatus should revolve at from thirty to forty revolutions per minute. The mixture is then filtered, and the phosphoric acid in 100 c.c. of the filtrate, or, in the case of precipitated phosphates, in 50 c.c., estimated by the molybdate or citrate method.

The filtrate frequently passes through the filter turbid, particularly in the case of precipitated phosphates; it is, therefore, advisable to use filter paper of the very best quality, such as is employed in the analysis of basic slag.

**3. Kellner's Method.**—This method has been proposed for the estimation of "citrate soluble" or "available" phosphoric acid in precipitated phosphates; practically only the dibasic phosphoric acid is determined.

Two and a half grams of the thoroughly ground sample are transferred to a capacious flask with 250 c.c. of Petermann's citrate solution and shaken in a rotating apparatus at a temperature of  $17^{\circ}5$ , similarly to the treatment of basic slags. The solution is then filtered off and 50 c.c. of the filtrate, = 0.5 g. substance, boiled for ten minutes with 20 c.c. of nitric acid; after allowing the solution to cool, and neutralising, the contained phosphoric acid is estimated as usual.

Petermann's citrate solution is prepared as follows:—173.2 g. of citric acid are dissolved in water, a solution of ammonium sulphate containing 40.75 g. of nitrogen gradually added, the mixture allowed to cool to  $15^{\circ}$ , and the whole made up to 1000 c.c. at  $15^{\circ}$ . The content of the ammonium sulphate solution is checked by titration and the composition of the mixture by the specific gravity which should be 1.082 to 1.083, and by the estimation of the contained ammonia which is determined by distilling 25 c.c. of the solution with magnesia.

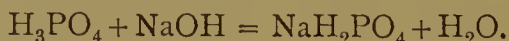
## E. ESTIMATION OF FREE PHOSPHORIC ACID

**1. Gravimetric Method.**—Ten grams of substance (superphosphate, etc.), dried at  $105^{\circ}$  to  $110^{\circ}$ , are rubbed up with absolute ether or alcohol, washed into a 500 c.c. flask, diluted to the mark with ether or alcohol, shaken for half an hour, and filtered. Fifty c.c. of the filtrate are taken, the ether or alcohol evaporated off, and the residue taken up with water; the phosphoric acid in this solution is then estimated as usual by the citrate method.

The substance may also be extracted with ether or alcohol, using a reflux condenser.

**2. Volumetric Method.**—The following method is due to the Union of German Manure Manufacturers.

A quantity of the aqueous extract of superphosphates, etc., corresponding to 1 g. of substance, is diluted with water in an Erlenmeyer flask to about 100 c.c., two or three drops of an aqueous solution of pure methyl orange (1:1000) added, and the solution titrated with sodium hydroxide until the red colour has changed to yellow. The sodium hydroxide should be standardised by a solution of pure phosphoric acid, the strength of which has been accurately determined, and should be titrated under the same conditions of dilution, etc., as obtain in the analysis, the acid solution being titrated with the alkali, not *vice versa*. The colour changes as soon as the primary salt has been formed from the phosphoric acid, according to the equation:—



It is recommended that after titration an excess of alkali be added to the superphosphate solution, the precipitate then filtered off, and the excess of alkali in an aliquot part of the filtrate titrated back with acid; the colour change is then more easily recognised. Addition of excess of alkali is certainly a source of error, as sodium hydroxide is taken up by the precipitate, and the extent of this combination increases with the excess of alkali added after the colour reaction with methyl orange. The alkali thus used up in the precipitation is not accounted for in titrating back if the precipitate is filtered off; too little acid is thus used to titrate back, and hence an erroneous result is obtained, and the amount of free phosphoric acid is over-estimated. It is, therefore, necessary to apply a correction, which will be constant for the same raw material and the same excess of alkali.

#### F. ESTIMATION OF PHOSPHORIC ACID SOLUBLE IN CITRIC ACID, IN BASIC SLAG

Manurial experiments which have been carried out at various experiment stations with basic slags from different sources have proved that the old basis on which the valuation of basic slag was carried out was inadequate, and that it was advisable not to value a basic slag exclusively according to its total content of phosphoric acid and "fine meal," but, in addition, to take into account its degree of solubility. Wagner worked out an analytical method founded on these experiments (treatment of basic slag with acid ammonium citrate solution)—a method adapted to determine the relative solubilities, and hence also the relative practical values of basic slags. This method

was thoroughly tested by the Union of Agricultural Laboratories of the German Empire, and it was agreed (1895) that the valuations of basic slag for commercial purposes should be founded on its content of "phosphoric acid soluble in citrate solution," and that estimations of total phosphoric acid and of "fine meal" should be discontinued.

Subsequently Wagner demonstrated that owing to the composition of the basic slag on the market having changed, the proportions of calcium and silica, or of easily decomposable silicate of calcium, had in general increased, and that in consequence the results of his analytical method no longer agreed with the relative effects of slags, as determined by small fertilisation experiments. He, therefore, proposed to use a 2 per cent. citric acid solution, instead of ammonium citrate solution, for the purpose of dissolving out the phosphoric acid of basic slag, and suggested the estimation of "phosphoric acid soluble in citric acid solution" by the following method. The results obtained by this later method show better agreement between solubility and manurial value than was the case when the previous solution was used.

For the estimation, 5 g. of basic slag are placed in a 500 c.c. flask into which 5 c.c. of alcohol have previously been placed. The flask is then filled up to the mark with dilute 2 per cent. citric acid solution, at a temperature of  $17^{\circ}5$ , the flask closed by a rubber stopper, and placed without delay in a rotating apparatus making thirty to forty revolutions per minute, then left for thirty minutes, and the mixture immediately filtered.

The phosphoric acid in the filtrate is then estimated either by the molybdate or citrate method, or by the Lorenz method.

**1. Molybdate Method.**—Fifty c.c. of the filtrate are placed in a beaker, treated with 80 to 100 c.c. of molybdate solution, and the mixture warmed to about  $65^{\circ}$  by placing it in a water-bath; the beaker is then taken out of the bath, and placed aside to cool. When cold, the mixture is filtered, the yellow precipitate carefully and thoroughly washed with 1 per cent. nitric acid, dissolved in about 100 c.c. of cold, 2 per cent. ammonia, 15 c.c. of magnesia mixture added to the ammoniacal solution, drop by drop, and with constant stirring, the beaker then covered with a glass plate and placed aside for two hours. The magnesium ammonium phosphate is then collected either in a Gooch crucible or on a filter paper, the precipitate thoroughly washed with 2 per cent. ammonia, dried, ignited over a Bunsen burner till the filter paper is completely incinerated (thirty to forty minutes), finally ignited for two minutes in a Rössler furnace, allowed to cool in a desiccator, and weighed.

It is a necessary condition that the yellow precipitate shall dissolve rapidly in cold, 2 per cent. ammonia, giving a perfectly clear solution. If the solution only becomes clear after standing for some time, the



following procedure must be adopted. The ammoniacal solution is precipitated by magnesia mixture, the precipitate collected on a filter, the beaker placed beneath the funnel, the precipitate then dissolved from the filter, and the latter washed by pouring about 100 c.c. of 0.5 per cent. hydrochloric acid through the filter; 20 c.c. of a mixture of one part of magnesia mixture and two parts of 20 per cent. ammonia are then added to the filtrate, drop by drop, and with constant stirring. The precipitate is then treated as described above (Estimation of phosphoric acid soluble in citric acid solution, in basic slags, by Wagner's Method).

Müller<sup>1</sup> has proposed a more simple form of the molybdate method, which consists in washing the yellow molybdate precipitate once by decantation with 1 per cent. nitric acid, bringing as little as possible of the precipitate on to the filter. The precipitate is then dissolved in 2 per cent. ammonia, and the filter washed seven times. Fifty c.c. of ordinary citrate solution (p. 394) are added, then 25 c.c. of magnesia mixture, and the mixture stirred with a glass rod in a stirring machine, or shaken in a shaking machine for ten minutes, the precipitate collected in a Gooch crucible, and dried and ignited as usual.

**2. Citrate Method.**—Wagner's earlier statements to the effect that the direct precipitation of phosphoric acid by magnesia mixture gives too high results when the silicic acid in solution exceeds a certain limit, have not been confirmed. Hence phosphoric acid in a citric acid solution of phosphate can be estimated much more rapidly and conveniently by direct precipitation with ordinary citrate solution and magnesia mixture.

Böttcher has found<sup>2</sup> that phosphoric acid soluble in citric acid solution can be correctly estimated by the ordinary citrate method without any modifications whatever, if the following precautions be observed. The precipitation must be carried out with freshly prepared solutions; the precipitate must be "shaken out" immediately after the citrate solution and the magnesia mixture have been added, and the shaking must be immediately followed by filtration. He has, therefore, proposed the following simple method, which has been tested and adopted by the Union of Agricultural Laboratories of the German Empire as an official method:—

Fifty c.c. of a fresh citric acid solution, prepared according to Wagner's directions, are treated with 50 c.c. of ordinary citrate solution (*cf.* p. 394) and 25 c.c. of magnesia mixture (prepared as given on p. 394). This mixture is shaken for thirty minutes in a rotation apparatus, filtered with the least possible delay through a Gooch crucible, the precipitate thoroughly washed with dilute (5 per cent.) ammonia, and then dried, ignited, etc., as usual.

<sup>1</sup> *Landw. Versuchs-Stat.*, 1896, 46, 47.

<sup>2</sup> *Chem. Zeit.*, 1897, 21, 168, 783, 993.

Wagner<sup>1</sup> has proposed precipitation by magnesia mixture containing citrate (cf. *infra*). The precipitate may be filtered either immediately, or after standing for two hours. Fifty c.c. of the citric acid solution of the phosphate are treated with 50 c.c. of magnesia-citrate mixture, the whole shaken or stirred for thirty minutes, and the estimation continued as above.

*Composition of the Reagents (Wagner).*

1. *Concentrated Citric Acid Solution (10 per cent.).*—Exactly 1 kg. of chemically pure, crystallised, non-effloresced citric acid is dissolved in water, the solution diluted to exactly 10 litres, and 5 g. of salicylic acid added.

2. *Dilute Citric Acid Solution (2 per cent.).*—Exactly one volume of the concentrated citric acid solution (1) is diluted with four volumes of water.

3. *Molybdate Solution.*—This may be prepared according to either of the following directions:—

(a) One hundred and twenty-five grams of pure molybdic acid are placed in a litre flask, suspended in about 100 c.c. of water, and dissolved by the addition of about 300 c.c. of 8 per cent. ammonia. Four hundred grams of ammonium nitrate are added to this solution, water added up to the mark, and the solution then poured into 1 litre of nitric acid of sp. gr. 1.19. The mixture is allowed to stand for twenty-four hours at about 35°, and then filtered.

(b) One hundred and fifty grams of chemically pure ammonium molybdate are placed in a litre flask, dissolved in water, 400 g. of ammonium nitrate added to the solution, which is then diluted to the mark with water and poured into 1 litre of nitric acid of sp. gr. 1.1. The mixture is allowed to stand for twenty-four hours at about 35°, and then filtered.

4. *Magnesia Mixture.*—One hundred and ten grams of pure, crystallised magnesium chloride and 140 g. of ammonium chloride are covered with 700 c.c. of aqueous ammonia (8 per cent.) and 1300 c.c. of water. The mixture is allowed to stand for several days, and then filtered.

5. *Magnesia-Citrate Mixture.*—Two hundred grams of citric acid are dissolved in 20 per cent. ammonia, the solution diluted to 1 litre with 20 per cent. ammonia, and mixed with 1 litre of magnesia mixture.

*Remarks on the above Method.*

1. The citric acid solution with which the basic slag is treated must, of course, be accurately of the strength given above, *i.e.*, it must contain accurately 20 g. of chemically pure, crystallised, non-effloresced

<sup>1</sup> *Chem. Zeit.*, 1897, 21, 905.

citric acid per litre. Its strength must be tested by titrating 25 c.c. with standard sodium hydroxide and phenolphthalein.

2. The citric acid solution to be used must have, as accurately as possible, the mean room-temperature of  $17^{\circ}.5$ ; deviations from this temperature, give rise to errors. The rotation apparatus must, therefore, be set up in a room of approximately constant temperature. The effect of deviations in the temperature may be counteracted by placing metal covers lined with felt over the 500 c.c. flasks.

3. It is to be noticed in addition that when 500 c.c. of citric acid are poured on to the basic slag in the flask, the slag is liable to ball itself together into small lumps, which withstand the moistening action of the solution for some time and stick to the bottom of the flask. Although this occurrence is rare, still attention should be paid to it, and in order to be certain of always avoiding the error to which it may give rise, 5 c.c. alcohol are poured into the 500 c.c. flask before the basic slag is weighed into it. Further, it is advisable to shake round after a portion (200 to 300 c.c.) of the citric acid has been added, so that nothing shall adhere to the bottom.

4. The substitution of a shaking machine for the prescribed rotation apparatus has proved to be inadmissible. Shaking machines differ in construction, and are not all equally effective, so that the results would not be consistent.

5. The rotation apparatus must not work at more than forty or less than thirty revolutions per minute, and the operation is to be continued for exactly half an hour. When this is complete the precipitate must be filtered immediately; if it be left to stand, an error in either direction may result.

6. Filtration must be accelerated as much as possible; it is best to use a folded filter paper of such a size that the whole of the liquid can be transferred at once to the filter, as soon as the undissolved residue has settled. Small and badly acting filters may become sources of error, owing to retardation of filtration. If the filtrate is at first turbid, it must be poured back on to the filter until a perfectly clear filtrate is obtained. It is not permissible to repeatedly return the filtrate to the filter, as this would unduly prolong the operation of filtration. Best quality filter paper must be used.

7. Careful attention must be paid to the absolute purity of the molybdic acid or ammonium molybdate used in preparing the molybdate solution.

8. Before using the molybdate solution its purity must be tested by means of disodium phosphate solution.

9. The mixture of citric acid solution and molybdate solution must be taken from the water-bath as soon as it has reached the prescribed temperature of  $65^{\circ}$ . Any appreciable prolongation of this digestion



may give rise to contamination of the precipitate by silicic acid. This is particularly liable to occur if the citric acid solution is not quite fresh and has been allowed to stand for six or twelve hours before adding the molybdate solution.

10. Contamination of the molybdate precipitate by silicic acid is recognised by the difficult solubility of the same in ammonia, giving rise to a turbid solution, which may only become clear after some time. When this is the case the magnesia precipitate must be reprecipitated, as described above.

11. The citric acid solution of basic slag undergoes little or no external change on standing, and even after some days will be either perfectly clear, or else only slightly turbid, without the formation of a precipitate. Nevertheless, a change takes place which is of great importance as regards the application of the direct method of precipitation, since the silicic acid, which goes into the solution, assumes a condition in which it is precipitated on addition of ammonia or ammoniacal citrate solution. This condition becomes increasingly pronounced from hour to hour; it is, therefore, necessary to precipitate the filtered extract with the least possible delay.

The precipitation of the silicic acid is facilitated by warming; the stirring or shaking of the precipitating mixture must, therefore, be conducted in a cool place (if necessary in a water-bath).

Naumann<sup>1</sup> has recommended the following method of estimating the phosphoric acid in the citric acid solution:—

One hundred c.c. of the filtered citrate solution are placed in an Erlenmeyer flask, 30 c.c. of concentrated nitric acid added, and the mixture evaporated down over a free flame to about 20 c.c.; the residue is boiled for about ten minutes with 25 c.c. of concentrated, arsenic-free sulphuric acid, in order to precipitate the silicic acid, then washed into a 250 c.c. flask, filtered, and 100 c.c. of this solution (=0.4 g. substance) precipitated by the usual citrate method. The precipitate crystallises well, so that it can be easily collected in a Gooch crucible.

Mach and Passou use the following, similar method:—

One hundred c.c. of the filtered basic slag solution are placed in a Kjeldahl flask, 30 c.c. of acid-mixture (see below) and one drop of mercury added, and the solution evaporated down on a wire gauze over an Argand burner to about 10 c.c.; the acid-mixture consists of twenty volumes of concentrated nitric acid mixed with ten volumes of concentrated, arsenic-free sulphuric acid. Towards the end, the flask must be repeatedly shaken round to prevent calcium sulphate caking on to it. The flame is removed, 20 c.c. of a 10 per cent. solution of common salt added, the liquid washed into a 200 c.c. flask, diluted

<sup>1</sup> *Landw. Versuchs-Stat.*, 1896, 47, 154.

to the mark, and filtered through a folded filter. One hundred c.c. of ordinary citrate solution (p. 394) are then added to 100 c.c. of the filtrate (=0.5 g. substance); when cold, this is treated with 25 c.c. of magnesia mixture, the solution shaken or stirred round, and filtered as usual through a Gooch crucible.

All these methods have now been superseded by Böttcher's equally simple and reliable method of direct precipitation with magnesia mixture (p. 406), which is much more expeditious.

**Note.**—The remarks made with regard to the Estimation of Nitrogen (p. 385) apply with equal force to the Estimation of Phosphoric Acid in all fertilisers. The processes given in the "Fertilisers and Feeding Stuffs (Methods of Analysis) Regulations, 1908," issued by the Board of Agriculture and Fisheries, are substantially described in the foregoing pages, but, as in the case of the nitrogen determination, it will in future be necessary in all cases in which the analyses are required for the purposes of the Act, to comply strictly with the provisions laid down by the Board. These, with some notes, are given at the end of the Section on "Feeding Stuffs," p. 469. (Smetham).

### 3. ESTIMATION OF POTASSIUM<sup>1</sup>

#### A. DETAILED METHOD

Solutions of manures containing sulphuric acid and phosphoric acid must be freed from these acids before the potassium can be estimated, but it is not necessary to separate the alkaline earths. Platinum chloride forms double salts with the chlorides of potassium, calcium, magnesium, barium, and strontium; of these, only potassium platini-chloride is insoluble in alcohol.

To estimate the soluble potassium salts, 10 g. of substance, which must pass through a 1 mm. sieve, are boiled for a quarter of an hour with 400 c.c. of water; when cold, the solution is diluted to exactly 500 c.c., filtered, 100 c.c. of the filtrate placed in a 500 c.c. flask, 5 to 10 c.c. of hydrochloric acid and 100 c.c. of water added, and the solution heated to boiling; the sulphuric acid is then precipitated by adding potassium-free barium chloride as long as a precipitate is formed, the mixture boiled for a short time, allowed to cool, diluted to the mark, and filtered. Two hundred and fifty c.c. of this filtrate are then placed in a 500 c.c. flask and warmed; if much phosphoric acid is present ferric chloride must be added; an excess of ammonia and ammonium carbonate solution are then added, the mixture allowed to cool, diluted to the mark, and filtered through a dry folded filter paper. Two hundred and fifty c.c. of the filtrate (=0.5 g. substance) are

<sup>1</sup> Cf. Vol. I., pp. 520 *et seq.*

evaporated to dryness in a platinum dish, and the residue heated over a wire gauze, at first gently, to avoid spitting, then more strongly, using an Argand burner, and finally, to a dull red heat, so as to volatilise all ammonium salts. Care must be taken to avoid volatilisation of potassium chloride at this stage. The residue is weighed in the dish, taken up with a little hot water, the solution filtered through a small filter into a porcelain dish, the filter and platinum dish thoroughly washed out, a few drops of pure hydrochloric acid added to the filtrate, which is then evaporated to dryness on the water-bath. Two to three c.c. of water are then added, and platinum chloride solution (1:20) to the amount of 3.5 c.c. to every 1 g. of salt obtained as residue in the platinum dish; this solution is then evaporated to a syrup on the water-bath in an ammonia-free atmosphere; when cold, a little 80 per cent. alcohol is added with stirring, then a further 50 to 60 c.c. of alcohol of the same strength, and the whole stirred. After standing for two to three hours the precipitate is filtered on a weighed filter paper, washed with 80 per cent. alcohol, and dried for two to three hours at 110° to 120°.

Filtering tubes, or Gooch crucibles fitted with asbestos, are preferable for the filtration.

The weight of the potassium platinichloride precipitate, multiplied by 0.1931, gives the weight of  $K_2O$  in 0.5 g. of the original substance, from which the percentage can be calculated.

### B. SHORTENED METHOD

Potassium can also be estimated in the Stassfurt potassium salts, such as kainite, potassium chloride, etc., by this method;<sup>1</sup> the result obtained, however, can only be considered reliable after the precipitate has been redissolved from the filter by hot water and the dried filter weighed again, owing to the fact that the precipitate of potassium platinichloride contains a certain amount of impurity, which would otherwise give too high a result. A Gooch crucible is well adapted for this purpose; the first precipitate of potassium platinichloride is collected in it, washed, dried, weighed, and then dissolved by hot water, the crucible washed, dried, and re-weighed, and the weight of impurity thus obtained.

To carry out the analysis, 250 c.c. of the aqueous solution of the potassium salts, prepared as above (p. 410), are placed in a 500 c.c. flask, 10 c.c. of hydrochloric acid added, and the solution boiled with potassium-free barium chloride solution.

An appreciable excess of barium chloride must be carefully avoided. Barium chloride solution of known strength (1:10) is added

<sup>1</sup> Fresenius, *Quantitative Analysis*, translated by C. E. Groves, 7th ed., 1900, vol. ii., p. 220.



to the boiling solution until further addition only produces a slight turbidity; the mixture is then boiled up again, allowed to settle till clear, and tested by the addition of one drop of barium chloride solution. If a precipitate is still formed a little more barium chloride solution is added, the mixture boiled, allowed to settle, and tested again; the point at which all the sulphuric acid is precipitated can be fairly sharply observed in the clear supernatant liquid. When no turbidity is caused by addition of barium chloride solution, a drop of dilute sulphuric acid is added in order to detect any excess of barium chloride. Alternate additions of sulphuric acid and barium chloride soon enable the operator to reach the point at which neither sulphuric acid nor barium chloride produce a precipitate; the operation is then complete.

When cold, the flask is filled to the mark, the solution filtered, 50 c.c. of the filtrate (= 0.5 g. substance) evaporated to dryness in a porcelain dish, the residue redissolved in about 10 to 15 c.c. of water, 10 c.c. of platinum chloride (1 : 20) added, and the solution evaporated to a syrup. The cold residue is taken up with a little 80 per cent. alcohol, rubbed fine with a pestle, a further 50 to 60 c.c. of 80 per cent. alcohol added, and the dish allowed to stand for two to three hours; the precipitate is then filtered off into a Gooch crucible, thoroughly washed with 80 per cent. alcohol, and dried at 110° to 120° till its weight is constant. After weighing, the potassium platinichloride is dissolved in hot water, the crucible thoroughly washed, first with hot water and then with alcohol, then dried and again weighed.

#### C. VOGEL AND HÄFFKE'S METHOD<sup>1</sup>

Fifty c.c. of the aqueous solution of the potassium salts (= 1.0 g. substance) are placed in a platinum dish and approximately neutralised by the addition of a few drops of ammonia; 20 c.c. of neutral ammonium carbonate solution are then added to precipitate the alkaline earths and magnesia. After standing for twelve hours, the precipitate is filtered off on a small filter, the dish and precipitate washed with 10 to 15 c.c. of the precipitant, and the filtrate evaporated to dryness in a platinum dish, which must, at first, be covered over. The residue is ignited to volatilise ammonium salts, taken up with hot water, and filtered through a small filter into a well-glazed, smooth porcelain dish, in which it is evaporated with platinum chloride solution. After the addition of one drop of hydrochloric acid and sufficient platinum chloride, the solution is evaporated on a water-bath which must be kept just boiling. The evaporation is continued until the liquid mass solidifies on cooling and no longer smells of hydrochloric acid. When

<sup>1</sup> *Landw. Versuchs-Stat.*, 1896, 47, 97.

perfectly cold, the residue is treated with 20 to 25 c.c. of a mixture of two parts of absolute alcohol and one part of ether; the crystals are rubbed fine with a small agate pestle and filtered, after standing for fifteen minutes. A porcelain Gooch crucible provided with an asbestos filter (*cf.* p. 394) is used for the filtration. The precipitate is thoroughly washed with the ether-alcohol mixture, dried, and the potassium platinichloride then reduced in a current of hydrogen. The crucible is allowed to cool in hydrogen, and is then washed with hot water to free the platinum from sodium sulphate and potassium chloride; the platinum is finally ignited and weighed.

This method is particularly adapted to the estimation of potassium in organic substances such as hay, straw, stable manure, poudrette, etc., since it avoids incineration and allows of the sulphuric acid solution obtained as in estimating nitrogen by Kjeldahl's method being used for the estimation. Fifty c.c. of this solution are first approximately neutralised by ammonia in a 200 c.c. flask, 25 c.c. of carbonate of ammonia solution added, and the further treatment carried out as described above.

#### D. PERCHLORIC ACID METHOD

The following alternative method is strongly recommended on account of its simplicity. An aqueous solution of the potassium salt is prepared in the usual way, and freed from sulphuric acid by means of barium chloride. One hundred c.c. of this solution (= 0.5 g. substance; where the percentage of potassium is high, 0.25 g. must be used) are evaporated to about 20 c.c. in a shallow glass dish; while still warm, 5 c.c. of a 20 per cent. perchloric acid solution are added. The amount of perchloric acid to be added amounts to from one and a half to one and three-quarter times the quantity necessary for the decomposition of all the salts present. The solution thus obtained is evaporated on the water-bath until the smell of hydrochloric acid can no longer be detected and white fumes of perchloric acid begin to escape. When cold, the residue is treated with 15 c.c. of 96 per cent. alcohol, and carefully rubbed down. After allowing to settle, the supernatant liquid is filtered through a Gooch crucible, the residue of potassium perchlorate then twice rubbed up with 96 per cent. alcohol containing 0.2 per cent. of perchloric acid, the washings decanted, the perchlorate transferred to the crucible, and thoroughly washed with alcohol containing 0.2 per cent. of perchloric acid. Finally, the precipitate is washed with the smallest possible quantity of 96 per cent. alcohol, to free it from perchloric acid, and dried at 120° to 130° for half an hour. The total volume of the filtrate should amount to about 75 c.c.

In treating superphosphates containing potassium and ammonia

the phosphoric acid and ammonia must first be removed as in the case of the platinum chloride method.

**Note.**—The “Fertilisers and Feeding Stuffs (Methods of Analysis) Regulation, 1908” apply, so far as the sale of potassic manures in the United Kingdom is concerned, to the estimation of potassium. As these regulations govern the ultimate sale of these commodities to the farmer, it seems probable that the processes therein prescribed must eventually form the basis of all contracts (Smetham).

The Regulations are given in detail at the end of the Section on “Feeding Stuffs” (p. 475).

#### 4. ESTIMATION OF FERRIC OXIDE AND ALUMINA

The estimation of ferric oxide and alumina is of great importance in connection with mineral phosphates used in the manufacture of superphosphates, since it gives an indication of the amount of phosphoric acid which can subsequently be reverted, *i.e.*, be rendered insoluble in water, but still be soluble in citrate solution, which has been adopted as a standard method by the Union of Agricultural Laboratories of the German Empire.

Of the many methods which have been proposed for this determination, that due to E. Glaser<sup>1</sup> is to be recommended.

The estimation is carried out as follows:—Five grams of the phosphate are dissolved, in the usual way, in a mixture of 25 c.c. of concentrated nitric acid (sp. gr. 1.2) and about 12.5 c.c. of hydrochloric acid (sp. gr. 1.12).

In English contracts for mineral phosphates it is usual to exclude the iron existing as pyrites from the determination of oxide of iron. With this end in view hydrochloric acid only must be used to decompose the phosphate, in which acid the pyrites is insoluble (Smetham).

The solution is diluted to 500 c.c., 100 c.c. of the filtrate (= 1.0 g. substance) placed in a 250 c.c. flask, 25 c.c. of sulphuric acid (sp. gr. 1.84) added, allowed to stand for five minutes with occasional shaking, and then about 100 c.c. of 95 per cent. alcohol are poured into the solution. The contents of the flask are then cooled, the flask filled up to the mark with alcohol, thoroughly shaken, filled up again with alcohol (since considerable contraction takes place), and again shaken. The liquid is filtered after standing for half an hour, 100 c.c. of the filtrate evaporated in a platinum dish till all the alcohol is driven off, the solution then poured into a beaker, 50 c.c. of water added, and then bromine to ensure the complete oxidation of the iron to the ferric condition, and the excess of bromine boiled off. Ammonia is next added until the solution reacts alkaline; to avoid much effervescence

<sup>1</sup> *Landw. Versuchs-Stat.*, 1892, 38, 305.



the boiling must be interrupted during this addition. The excess of ammonia is then boiled off. When cold, the precipitate is filtered off, washed with hot water, ignited and weighed; it consists of ferric and aluminium phosphates. Half the weight thus obtained is regarded as representing the  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ . (This proportion is only a convention. In accurate tests, the precipitate should be analysed and the  $\text{Fe}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$  determined. The  $\text{Al}_2\text{O}_3$  is obtained by difference) (Smetham).

Crispo's method, though frequently recommended, is very complicated, lengthy, and by no means free from objections.

It is in many cases important to know the separate percentages of ferric oxide and alumina, so as to be able to study the influence of each constituent on the manufacture; von Grueber<sup>1</sup> has recommended the following method for this purpose:—

Ten grams of the mineral phosphate or superphosphate are dissolved, in a porcelain dish, in 100 c.c. of water and 20 c.c. of concentrated hydrochloric acid, and the solution evaporated to dryness to separate the silica. The residue is taken up with very dilute hydrochloric acid, the contents of the dish washed into a 500 c.c. flask, diluted to the mark, thoroughly mixed, and filtered through a folded filter. The filtrate serves for the estimations of phosphoric acid, ferric oxide, and alumina.

(a) *Alumina*.—Fifty c.c. of the acid solution (= 1.0 g. substance) are placed in a 200 c.c. flask and approximately neutralised with 20 per cent. sodium hydroxide solution; a further 30 c.c. of the same sodium hydroxide solution are added, the mixture heated to boiling and left to stand in a warm place for about ten minutes, with frequent shaking. When cold, the solution is diluted to the mark, thoroughly mixed, and filtered through a folded filter. One hundred c.c. of the filtrate (= 0.5 g. substance) are just neutralised with hydrochloric acid, a slight excess of ammonia added, and the mixture heated to boiling. The aluminium phosphate thus precipitated is filtered off, washed with hot water till the filtrate no longer contains chloride, dried, ignited, and weighed. The weight of  $\text{AlPO}_4$  found, multiplied by 41.8, gives the percentage of  $\text{Al}_2\text{O}_3$ .

(b) *Ferric Oxide*.—One hundred c.c. of the filtrate (= 2.0 g. substance) are placed in a 200 c.c. flask, reduced with zinc and sulphuric acid, the solution diluted to the mark and thoroughly mixed.

A mixture of 200 c.c. of water and 50 c.c. of 20 per cent. sulphuric acid are placed in a beaker, to this 50 c.c. of the reduced iron solution added, and then titrated with potassium permanganate; the latter may be either semi-normal, or deci-normal, or merely empirically standardised by metallic iron. After this first titration another 50 c.c. of reduced iron solution are added to the liquid in the beaker and the

<sup>1</sup> *Landw. Versuchs-Stat.*, 1897, 49, 58.

titration repeated; then a third 50 c.c. are added, and if necessary, the operation is repeated a fourth time; in general, the third titration will agree accurately with the second, and the figure thus obtained gives the percentage of iron.<sup>1</sup>

M. Hauffe's method<sup>2</sup> also gives good results and may be applied in all cases, even to the estimation of minute quantities of iron in phosphates and superphosphates. This applies also to F. Lichtschlag's method,<sup>3</sup> in which the total alumina and total iron are estimated separately; this method permits of the separate sesquioxides being very expeditiously estimated, even in presence of difficultly soluble aluminium silicates and pyrites. Stutzer's method<sup>4</sup> is also still frequently used.<sup>5</sup>

Glaser's method, as modified by R. Jones,<sup>6</sup> was adopted by the Fifth International Congress of Applied Chemistry (Berlin, 1903) for the estimation of iron and alumina.

## 5. ESTIMATION OF FLUORINE

The estimation of fluorine in minerals is one of the more difficult analytical determinations particularly in presence of carbonic acid, chlorine, and organic substances. Von Grueber<sup>7</sup> regards M. Hauffe's modified form of H. Offermann's method<sup>8</sup> as the most reliable; this is founded on the conversion of the fluorine present into silicon fluoride, the decomposition of the latter by water and the titration of the hydrofluosilicic acid formed with normal potassium hydroxide.

The sample must be rendered anhydrous if accurate results are to be obtained. Raw phosphates must be dried at 150° to 170°, or gently ignited; superphosphates are weighed out into a small platinum dish, milk of lime added till the mixture is distinctly alkaline, the water evaporated off on the water-bath, and the residue dried and gently ignited. When cold, the residue is ground fine and transferred to a flask by means of a dry funnel; the funnel and dish are then repeatedly "rinsed" with finely powdered, ignited quartz.

The sulphuric acid to be used must, as nearly as possible, be pure monohydrate. Every part of the apparatus must be absolutely dry and the glass tubes must be in contact at the joint. The apparatus is arranged as follows (Fig. 66):—A gas holder A drives air into the

<sup>1</sup> Cf. Vol. I., p. 102; also the following papers in regard to the titration with permanganate in hydrochloric acid solution:—W. C. Birch, *Chem. News*, 1909, 99, 61, 73; J. A. N. Friend, *J. Chem. Soc.*, 1909, 95, 1228; G. C. Jones and J. H. Jeffery, *Analyst*, 1909, 34, 306.

<sup>2</sup> *Chem. Zeit.*, 1897, 21, 894. <sup>3</sup> *Ibid.*, 1897, 21, 264. <sup>4</sup> *Z. angew. Chem.*, 1890, 3, 615.

<sup>5</sup> A full description of the methods for the estimation of Oxide of Iron and Alumina as usually applied in England is given in *J. Soc. Chem. Ind.*, 1893, 12, 112.

<sup>6</sup> *Z. angew. Chem.*, 1891, 4, 3; *J. Soc. Chem. Ind.*, 1891, 10, 387.

<sup>7</sup> *Methode zur Untersuchung der Kunstdüngemittel*, 1898, Vol. II.

<sup>8</sup> *Z. angew. Chem.*, 1890, 3, 615.

wash-bottle B, containing an alkaline solution of potassium permanganate; from B the air passes through the wash-bottle C charged with concentrated sulphuric acid, and the absorption cylinders D and E filled respectively with granular soda-lime and small pieces of fused calcium chloride. These portions of the apparatus must be of large size, so that they may serve for several fluorine estimations without being refilled. The flask F (capacity 300 to 400 c.c.) serves for the decomposition of the mineral; it is closed by a trebly bored stopper through which pass a separating funnel with a long stem and two glass tubes bent at right angles. The current of dry air enters by the longer of these two tubes, the shorter conducts away the mixture of air and silicon fluoride. The flask G is not connected to the apparatus; it contains as much concentrated sulphuric acid as is subsequently allowed to flow into F and is provided with a thermometer; this flask serves

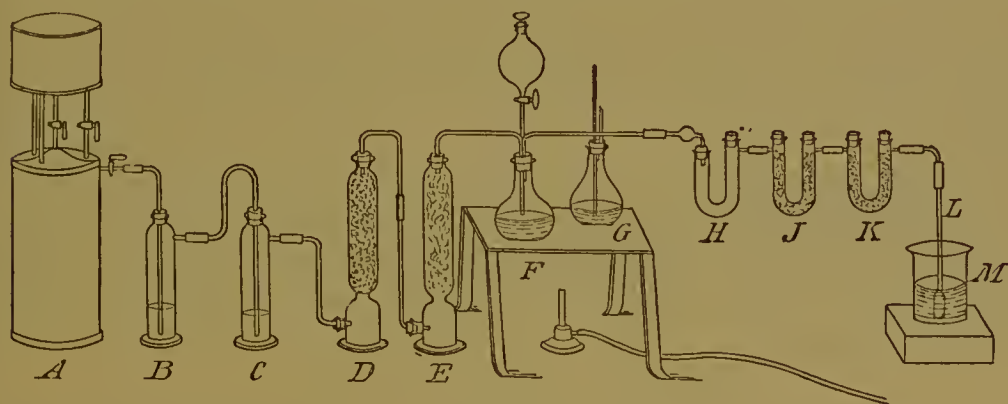


FIG. 66.

chiefly to determine and regulate the proper temperature for the decomposition.

The two flasks, F and G, are placed on an iron plate covered with wire gauze, in such a way that both are equally heated. The dry, empty U-tube H is connected on the one hand to the decomposition flask F, on the other hand to the tube J, filled with freshly fused calcium chloride, which must not have an alkaline reaction. The tube K contains pumice soaked in anhydrous copper sulphate, and a little mercury is placed in the beaker M. A 15 or 20 c.c. pipette, L, cut through the middle and firmly clamped in a retort stand, serves as the delivery tube; the edges must be ground as smoothly as possible after cutting, and this wider end of the tube is dipped 1 or 1.5 mm. deep in the mercury.

The whole apparatus is first tested to make sure it is air-tight. The prepared substance is then placed in the flask F, together with fifteen to twenty times its weight of ignited quartz powder or finely powdered sand; if sand be used it must be purified by treatment with



concentrated sulphuric and then hydrochloric acid, and thoroughly washed and ignited. The substance and quartz are mixed by shaking round, and the flask is placed in position; the beaker M is then filled with water, the amount being adapted to the probable content of fluorine (from 50 to 200 c.c.). An aqueous extract of quillaia is then added, made by boiling 1 g. of quillaia in 100 c.c. of water; twelve to sixteen drops of this extract are added to every 100 c.c. of water in the beaker. This provision causes the formation of a slight film of foam on the surface of the water when air is bubbled through, and thus ensures that the largest air bubbles give up the whole of their silicon fluoride to the water in M before bursting.

A current of air is then passed through the apparatus, and 50 to 60 c.c. of pure, concentrated, cold sulphuric acid are allowed to flow into the flask F from the separating funnel; the flask is then slowly heated to  $150^{\circ}$  to  $155^{\circ}$ , and, when decomposition is complete, is allowed to cool, air being passed through the whole apparatus for another hour. The contents of the beaker M are then titrated while hot with  $N/1$  or  $N/2$  potassium hydroxide, litmus solution or phenolphthalein being used as indicator.

To make sure that the whole of the silicon fluoride has been driven out of the apparatus, the tube L may be replaced by a fresh one, and air conducted through the apparatus, with fresh water in M, for another half hour; the second portion of water is then titrated. 1 c.c.  $N/1$  KOH = 0.019 g. F.

## II.—SPECIAL DIRECTIONS FOR THE EXAMINATION OF INDIVIDUAL MANURES

The following methods and directions have, in the main, been agreed upon by the Union of Agricultural Laboratories of the German Empire.

### I. PREPARATION OF SAMPLES IN THE LABORATORY, AND GENERAL DETERMINATIONS

1. Dry samples of phosphates or other artificial manures should be sifted and then mixed, if possible.

2. In the case of moist manures, where the above is not possible, preparation must be limited to careful and thorough mixing by hand.

3. The samples must be weighed on arrival, and the various specimens must be carefully separated. Half of each sample is prepared for analysis; the other half, up to 1 kg., is preserved in the unprepared state in tightly closed bottles, in a cool place, for three months, counting from the day of despatch of the analyst's report. This does not apply to those cases in which other conditions are decided

upon, either by special contract with the vendor of the manures in question, or by some other agreement.

4. In the case of mineral phosphates and bone black, estimations of the percentage of moisture at  $105^{\circ}$  to  $110^{\circ}$  must be shown. Ammonia must also be determined in the case of samples which lose ammonia in any form during drying.

5. Whenever samples have to be referred, it should be made a rule to send to the chemists concerned only carefully selected average samples of at least 250 to 500 g. weight, packed in tightly closed glass vessels.

6. The weight of the sample received must be stated in the certificate of analysis.

7. In the case of substances which alter their percentage of moisture during pulverisation, moisture must be estimated in both fine and coarse substance; the result of the analysis must be re-calculated on the basis of the original coarse substance.

8. The water-soluble and total phosphoric acid may be estimated in special cases by the molybdenum method, by the direct citrate method, or by the Lorenz method.

9. The limits allowed to the vendor are 0.5 per cent. phosphoric acid, 0.25 per cent. nitrogen, and 0.5 per cent. potash; and the analytical limits, 0.3 per cent. phosphoric acid in all forms, 0.2 per cent. nitrogen in all forms, and 0.3 per cent. potash.

## 2. ESTIMATION OF MOISTURE

To estimate moisture in superphosphates,<sup>1</sup> 10 g. of substance are heated for three hours in a drying oven to  $100^{\circ}$ ; the loss of weight is taken as moisture. In the case of other substances, 10 g. are weighed out and dried at  $105^{\circ}$  to  $110^{\circ}$  till the weight is constant.

## 3. EXAMINATION OF RAW PHOSPHATES

### A. MINERAL PHOSPHATES

*(Phosphorite, Apatite, Coprolite, and Mineral Phosphates generally.)*

1. *Moisture*.—Ten grams of substance are dried at  $105^{\circ}$  to  $110^{\circ}$  till the weight is constant.

2. *Phosphoric Acid*.—The substance is powdered as finely as possible in an agate mortar, and 5 g. boiled for half an hour in a 500 c.c. flask, either with 50 c.c. of aqua regia (consisting of three parts hydrochloric acid (sp. gr. 1.12) and one part nitric acid (sp. gr. 1.25)), or with a mixture of 20 c.c. of nitric acid (sp. gr. 1.42) and 50 c.c. of sulphuric

<sup>1</sup> Landw. Versuchs-Stat., 1890, 38, 306.

acid (sp. gr. 1.8). The solution is then diluted with water and, when perfectly cold, diluted to the mark; it is then filtered and 50 c.c. (=0.5 g. substance) taken for the estimation of the phosphoric acid by the citrate, molybdate, or Lorenz method (*cf.* pp. 389, 393, and 397).

To estimate phosphoric acid by the citrate method, 50 c.c. of the clear filtrate (=0.5 g. substance) are treated with 100 c.c. of citrate solution (p. 393); after cooling, 25 c.c. of magnesia mixture are added, and the precipitate filtered in a Gooch crucible, after shaking or stirring for half an hour.

If aqua regia be used to dissolve the raw phosphate, the silica must be separated if an accurate result is to be obtained. If sulphuric acid be used as solvent, the silica remains undissolved or separates in an insoluble form on boiling.

3. *Carbon dioxide*.—Four to five grams of substance are used, and the carbon dioxide estimated either in Scheibler's apparatus or gravi-

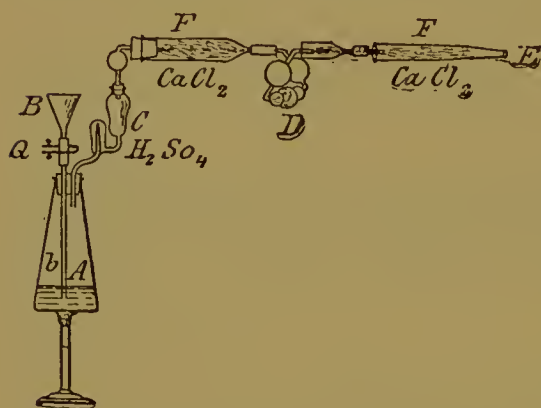


FIG. 67.

metrically in that of Geissler or Bunsen. The apparatus represented in Fig. 67 may be used with advantage, the arrangement of which is obvious. From 1 to 3 g. of substance are weighed out, according to the content of carbon dioxide, washed into the flask A (about 300 c.c. capacity) with a little freshly boiled water, the apparatus tested to ensure the joints being air-tight, and about

30 c.c. of phosphoric acid (sp. gr. 1.3) then allowed to flow in from the funnel B, and the pinch-cock Q immediately re-closed. The flask A is first heated with a small flame, and the liquid finally boiled to drive out all the carbon dioxide. The pinch-cock Q is then opened, an aspirator attached to E, and about 2 to 3 litres of air sucked through the apparatus; the air must pass through a tube containing solid potassium hydroxide before entering A. The potash bulbs, D, are weighed both before and after the experiment, and the percentage of carbon dioxide calculated from their increase in weight.

Carbon dioxide can also be accurately and rapidly estimated either by means of Lunge's calcimeter or by Lunge and Rittener's method.<sup>1</sup>

4. *Ferric oxide and Alumina* are estimated as described on p. 414.

<sup>1</sup> *Cf.* Vol. I., pp. 149, 153, and 514.



## B. PHOSPHATIC GUANOS

(*Baker Island guano, Malden Island guano, and similar Phosphates.*)

1. *Moisture*.—Ten grams of substance are dried at  $105^{\circ}$  to  $110^{\circ}$  till the weight is constant.

2. *Total Phosphoric Acid*.—Ten grams of finely powdered substance are boiled with acid for half an hour in a 500 c.c. flask; the acid may either be 50 c.c. aqua regia (made up of three parts hydrochloric acid (sp. gr. 1.12) and one part nitric acid (sp. gr. 1.25)), or a mixture of 20 c.c. of nitric acid (sp. gr. 1.42) with 50 c.c. of sulphuric acid (sp. gr. 1.8). When cold, the solution is diluted to the mark, filtered, and 50 c.c. (= 1 g. substance) used to estimate phosphoric acid by the citrate, molybdate, or Lorenz method.

3. *Nitrogen*.—There is very little nitrogen in these manures; if it is required to be estimated 1 g. of substance are treated according to the Jodlbauer (p. 378) or Förster method (p. 379).

4. *Carbon Dioxide*.—The method is the same as for mineral phosphates (p. 420).

5. *Ash and Sand*.—Five grams of substance are incinerated in a platinum crucible, and the residue weighed. The ash is then washed into a beaker or Erlenmeyer flask, boiled with 20 c.c. of hydrochloric or nitric acid for from a quarter to half an hour, the solution diluted and filtered, the filter thoroughly washed with hot water, and the residue dried, ignited in a platinum crucible, and weighed.

## C. BONE PHOSPHATES

(*Bone Charcoal, Bone Ash, Precipitated Bone Phosphate.*)

1. *Moisture*.—Ten grams of substance are dried at  $105^{\circ}$  to  $110^{\circ}$  till the weight is constant.

2. *Phosphoric Acid*.—The estimation is carried out as in the case of Phosphatic Guanoses (p. 421).

3. *Nitrogen*.—Only traces of nitrogen are present in these substances, and it is not customary to state the quantity in commercial analyses. If an estimation be desired, Kjeldahl's method (p. 378) is employed, using 1 g. of substance.

4. *Carbon Dioxide* is estimated as in mineral phosphates (p. 420).

5. *Insoluble Constituents*.—Five grams of substance are dissolved in 20 c.c. of aqua regia, the solution boiled for half an hour, diluted with water, filtered through a small filter, which is then washed with hot water until it no longer contains chloride, ignited and weighed.

6. *Free Lime* (CaO).—Caustic lime often occurs in burnt bones. It is best determined by taking the difference between two carbon dioxide

estimations, the first of which is made on the original substance, and the second on a sample prepared by repeatedly moistening the substance with a concentrated solution of ammonium carbonate and then heating it till the latter volatilises; it must not be ignited. The amount of caustic lime present is calculated from the difference between these two estimations.

#### D. PRECIPITATED PHOSPHATES

Precipitated phosphates are prepared from basic slag, bone meal, bone ash, and mineral phosphates; the precipitated phosphates prepared from basic slag can easily be identified by the manganese they contain.

These materials are dissolved in dilute hydrochloric acid, milk of lime added to the solution, the precipitate separated in a filter-press and dried. If the drying temperature is not too high, the phosphoric acid remains in the form of dibasic calcium phosphate. The value of a precipitated phosphate is determined by its total content of phosphoric acid and the percentage of phosphoric acid soluble in citrate solution.

1. *Total Phosphoric Acid*.—Five grams of substance are boiled with 50 c.c. of aqua regia, and the solution treated as described above.

2. *Phosphoric Acid soluble in Citrate Solution*.—This is determined by Petermann's method (p. 400).

3. *Ferric Oxide and Alumina*.—These estimations, if required, are carried out by Glaser's method (p. 414).

#### 4. EXAMINATION OF SUPERPHOSPHATES

1. *Moisture*.—Ten grams of superphosphate are dried in the oven for three hours at 100°; the loss in weight gives the moisture.

2. *Phosphoric Acid soluble in Water*.—The superphosphate is extracted as follows:—Twenty grams are placed in a litre flask, 800 c.c. of water poured in, and the flask continuously and vigorously shaken for thirty minutes. The solution is then diluted to the mark with water, the liquid vigorously shaken, and filtered immediately.<sup>1</sup>

The shaking is effected by means of a special shaking or rotation apparatus, worked by hand or by any kind of motor; one hundred and fifty revolutions per minute is recommended as the standard speed for the shaking apparatus; for the rotation apparatus, *cf.* p. 403.

The determination of the phosphoric acid soluble in water may be done either volumetrically by the uranium method (p. 387), or gravimetrically by the molybdate (p. 389), citrate (p. 393), or Lorenz method (p. 397).

In the citrate method, 50 c.c. of the clear aqueous filtrate

<sup>1</sup> *Landw. Versuchs-Stat.*, 1897, 49, 29.

(= 1 g. substance) are treated with 50 c.c. of citrate solution prepared according to the directions on p. 394, 25 c.c. of magnesia mixture (p. 394) then added, the mixture shaken for half an hour, filtered through a Gooch crucible, and the latter ignited and weighed (*cf.* p. 393). In the Lorenz method, 10 c.c. (= 0.2 g. substance) of the solution are made up to 50 c.c. with the nitric-sulphuric acid solution, and the estimation conducted as described above.

Solutions of double superphosphates must be boiled with nitric acid before precipitating the phosphoric acid; this converts any pyrophosphoric acid which may be present into ortho-phosphoric acid; 10 c.c. of concentrated nitric acid are added for 25 c.c. of solution.

Twenty-five c.c. of the aqueous solution (= 0.5 g. substance) are diluted with 50 to 75 c.c. of water, 10 c.c. of concentrated nitric acid (sp. gr. 1.4) added, and the solution heated for an hour on the sand-bath; excess of ammonia is added, the solution just acidified by a few drops nitric acid, and, when cold, 50 c.c. of citrate solution and 25 c.c. of magnesia mixture added; the further treatment is the same as in the case of superphosphates. The precipitate must be ignited for about ten minutes in a Rössler furnace.

3. *Phosphoric Acid soluble in Citrate Solution.*—Only a small quantity is present in superphosphates as a rule, and it is, therefore, rarely estimated; if, in exceptional cases, the determination be required, the substance must be treated by Petermann's method, as described on p. 400.

The percentage of phosphoric acid soluble in citrate solution in superphosphates, as given by Petermann's method, must be determined and stated separately; the term "soluble in citrate" must not be used to denote the sum of the phosphoric acid soluble in water and that soluble in citrate solution.<sup>1</sup>

4. *Total Phosphoric Acid.*—This is estimated as in the case of Phosphatic Guanos (p. 421).

## 5. EXAMINATION OF BASIC SLAGS

Basic slags which appear to contain coarser particles may be sifted through a 2 mm. sieve; the coarse, agglomerated particles remaining on the sieve are broken up by applying slight pressure while they are still on the sieve. Phosphoric acid is then estimated in the portion which passes through the 2 mm. sieve, the coarser particles being taken into account in calculating the result.

In the estimation of the phosphoric acid in basic slags it is customary in England to state the result on the whole sample as received.

<sup>1</sup> Cf. *Landw. Versuchs-Stat.*, 1897, 49, 60.



1. *Total Phosphoric Acid*.—According to Loges,<sup>1</sup> the slag must be decomposed by concentrated sulphuric acid.

Ten grams of substance are placed in a 1000 c.c. flask, moistened with a little water, and shaken round; 5 c.c. of dilute sulphuric acid (1:1) are added, and the thick pasty mass thus formed vigorously shaken round, so that nothing sticks to the bottom, and 50 c.c. of concentrated sulphuric acid then slowly added to this almost solid mass; the mixture is well agitated, and heated with frequent shaking for a quarter to half an hour on a wire gauze or asbestos till white fumes are evolved and a thin uniform paste is obtained. This is carefully diluted with water before it has completely cooled, the flask well shaken, cooled, filled to the mark, and the solution then filtered through a double folded filter. If the filtrate is allowed to stand for some time a quantity of calcium sulphate will separate out, owing to the decomposition of acid calcium sulphate; this, however, does not influence the accuracy of the results.

If phosphoric acid is to be estimated by the citrate method, 50 c.c. of the filtrate (= 0.5 g. substance) are treated with 100 c.c. of ordinary citrate solution, cooled, and 25 c.c. of magnesia mixture added. Aqua regia and nitric acid must not be used as solvents, since they dissolve phosphide of iron and oxidise it to phosphoric acid; hydrochloric acid must also be excluded as solvent, since it dissolves all impurities and foreign constituents of the slag; these accompany the magnesia precipitate, and the results obtained are too high. The solution is shaken for half an hour, filtered, the precipitate ignited, and weighed when cold. For Lorenz's method, 15 c.c. (= 0.15 g. substance) are taken.

If phosphoric acid is to be estimated by the molybdate method, 50 c.c. of the filtrate are treated with 100 c.c. of molybdate solution (p. 389) and the phosphoric acid determined as usual (p. 392).

2. *Phosphoric Acid soluble in Citric Acid Solution*.—Basic slags are now almost exclusively sold according to the percentage of phosphoric acid soluble in citric acid solution, and the price is regulated by this percentage. Hence, if a knowledge of the total phosphoric acid is not particularly required, only that soluble in citric acid is estimated, the usual method being that by direct precipitation described on p. 406.

In the case of arbitration analyses, in which the estimation of phosphoric acid soluble in citric acid in basic slags is concerned, the direct precipitation method of Böttcher should be used.<sup>2</sup>

Recently, basic slags have frequently been found to contain a high percentage of silica; in such cases the results of the direct method are very liable to be too high, so that every slag must first be tested for

<sup>1</sup> *Landw. Versuchs-Stat.*, 1888, 35, 2; 1894, 43, 424.

<sup>2</sup> Cf. p. 473; The Fertilisers and Feeding Stuffs (Methods of Analysis) Regulations, 1908.

silica by the following method, described by O. Kellner and O. Böttcher:<sup>1</sup>—Fifty c.c. of the citric acid solution are boiled for about a minute with 50 c.c. of ammoniacal citrate solution, and then placed aside for five to ten minutes. If a precipitate separates which is not completely soluble in hydrochloric acid, the amount of soluble silicic acid present will be liable to vitiate the results of Böttcher's direct precipitation method. The following ammoniacal citrate solution is used:—Eleven hundred grams of citric acid and 4000 g. of 24 per cent. ammonia, dissolved in water and diluted to 10 litres. If the presence of silica is indicated by this preliminary test, it must be separated as follows:—Seven and a half c.c. of hydrochloric acid (sp. gr. 1.12), or 5 c.c. of fuming hydrochloric acid, are added to 100 c.c. of the citric acid extract, and the solution evaporated on the water-bath till it forms a syrup and no longer smells of hydrochloric acid. This residue, while still hot, is thoroughly stirred up with 1.5 to 2.0 c.c. of hydrochloric acid (sp. gr. 1.12), dissolved in a little water, transferred to a 100 c.c. flask, diluted to the mark, and filtered; 50 c.c. of the filtrate are used to estimate the phosphoric acid by the direct method.

Usually, a normal slag with a very high percentage of silica, as shown by the separation of silica in the above preliminary test, will give accurate results by the direct method without the separation of the silica, provided that all operations follow each other with the least possible delay, and that each is conducted as rapidly as possible.

In the case of slags low in iron which give clear citric acid solutions, free from green colour (*e.g.*, Wolter phosphate, etc.), the silica must always be separated, since the direct method gives too high figures in such cases. Weibull<sup>2</sup> states that an addition of 0.1 g. of ferric chloride to 50 c.c. of the citric acid extract prevents the precipitation of silicic acid.

P. Wagner prevents the separation by the addition of 10 c.c. of 20 per cent. ferrous chloride solution to 1 litre of citrate-magnesia mixture, and then treats 50 c.c. of the phosphate solution with 50 c.c. of this iron-citrate-magnesia mixture. He has proposed the following method for the estimation of citrate-soluble phosphoric acid in basic slags, irrespective of whether the content of silica is considerable or not.

One hundred c.c. of the citric acid extract is treated with 50 c.c. of a citric acid-magnesia mixture made up as follows:—Two kilograms of citric acid and 400 g. of ammonium chloride are placed in a 10 litre flask with 2 litres of water, and 5 litres of 20 per cent. ammonia added; the flask is corked and allowed to stand till solution is complete; 550 g. of magnesium chloride are then added, and the whole made up to 10 litres. The extract, together with the added citric acid-magnesia mixture, is

<sup>1</sup> *Chem. Zeit.*, 1902, 26, 1151.

<sup>2</sup> *Ibid.*, 1902, 26, 297.

placed in a 200 c.c. flask, heated gently for 15 minutes until the silica has separated, the contents of the flask mixed so as to make the silica collect and settle, and the heating then continued to incipient boiling. After allowing to cool, 25 c.c. of nitric acid of sp. gr. 1.124 are added, and the flask allowed to stand for half an hour; during this period the contents of the flask are shaken round a few times. The flask is then filled up with water, a rubber stopper inserted, and the whole vigorously shaken so as to cause the silica to collect in a finely divided state. The solution is then filtered off, 100 c.c. of the filtrate (=0.5 g. substance) treated with 50 c.c. of 10 per cent. ammonia, and shaken for half an hour in a Stutzer's apparatus. The precipitate is then filtered, either at once or after standing for several hours, and treated as usual.

Lorenz's method (p. 397) can also be applied to the analysis of all basic slags, as its accuracy is not affected by the presence of silica.

3. *Lime, etc.*—The estimation of the total lime in basic slag requires great care, and is best effected by Hollemann's method.<sup>1</sup> Fifty c.c. of the hydrochloric acid solution of the sample (containing 1 g. substance) are concentrated to a small bulk, and then 20 c.c. of neutral ammonium oxalate solution (1:3) are stirred in; the mixture is digested on the water-bath until the precipitate is a pure white and free from lumps; this is generally attained in about ten minutes. The precipitate is then filtered, washed with hot water till the filtrate is free from oxalic acid, redissolved in the smallest possible quantity of concentrated hydrochloric acid, the solution concentrated if necessary to 25 c.c., and treated with 10 c.c. of sulphuric acid (1:3) and 150 c.c. of 96 per cent. alcohol. The precipitate is filtered off after standing for three hours, washed with alcohol till the filtrate is free from acid (as shown by methyl orange), and ignited; the lime is thus weighed as calcium sulphate.

Other constituents, such as manganese, iron, and magnesia, are estimated in the hydrochloric acid solution in the usual way.

A by no means negligible quantity of the lime is present in the free state; if this is to be estimated, 2 g. of substance are shaken with 200 c.c. of 10 per cent. sugar solution in a 300 c.c. flask, the solution diluted to the mark, filtered, and the calcium precipitated in an aliquot part of the filtrate by ammonium oxalate; the calcium oxalate may be either titrated with permanganate or estimated gravimetrically.<sup>2</sup>

4. *Silicic Acid and Sand.*—Five grams of the slag are digested with 20 to 25 c.c. of concentrated hydrochloric acid on the water-bath, evaporated to dryness, and the residue dried in the oven at 120° to 130°, so as to separate the silica. The dry residue is taken up with water containing a little hydrochloric acid, filtered, the residue washed with hot water, dried, ignited, and weighed as silica plus sand.

<sup>1</sup> *Chem. Zeit.*, 1892, 16, 1471.

<sup>2</sup> *Cf. J. Hendrick, J. Soc. Chem. Ind.*, 1909, 28, 775.



If the sand is to be estimated separately the weighed residue is extracted by boiling with a solution of sodium carbonate containing a little sodium hydroxide, the sand filtered off, washed with hot water, and weighed.

5. *Specific Gravity*.—The specific gravity of basic slag varies from 3.00 to 3.33; it is determined, as in the case of cement, by means of Schumann's volumeter.<sup>1</sup> The following method, due to Loges, may also be used:—Twenty grams of the slag are placed in a 50 c.c. flask and alcohol added from a burette; the flask is then shaken or tapped to remove air-bubbles, and filled to the mark.

6. *Fine Meal*.—Now that basic slags are no longer sold according to their total content of phosphoric acid, but exclusively according to the percentage of phosphoric acid soluble in citric acid solution, the determination of fine meal has become superfluous; the effective value of a slag can be judged solely from its percentage of phosphoric acid soluble in citric acid solution. If in an exceptional case the determination of fine meal should be required, it is conducted as follows<sup>2</sup>:—Fifty grams of the slag are placed on a sieve of not less than 20 cm. diameter, and of 10,000 meshes to the sq. in.;<sup>3</sup> the sieve is shaken for fifteen minutes by hand, or in a suitable shaking apparatus. The difference between the 50 g. taken and the weight of the residue remaining on the sieve is taken as the percentage of the fine meal.

7. *Identification of Adulterations in Basic Slags*.—The examination for adulterations has also really become unnecessary by the introduction of the content of available phosphoric acid (*i.e.*, that soluble in citric acid) as the basis of valuation. This is at any rate the case with adulteration with raw phosphates; such materials as phosphorite, Redonda phosphate, etc., which were formerly used to adulterate, are almost or completely insoluble in a 2 per cent. citric acid solution, so that such additions no longer pay.

If, nevertheless, it is required to examine a slag for adulteration, the moisture is first determined; 5 g. of the substance are heated for three hours in a platinum dish in the drying oven at 108°, and then ignited for fifteen minutes. Pure basic slag only contains traces of water; hence, if a slag loses appreciably more than 0.5 per cent. in weight on ignition it should be considered suspicious and further examined. The presence of a large amount of Redonda phosphate or of precipitated phosphate can be recognised by a specific gravity determination; liquids suited to effect a separation are bromoform (sp. gr. 2.775), solution of mercuric iodide in potassium iodide, and a solution of cadmium boro-tungstate (sp. gr. 3.3). Richter and Förster<sup>4</sup> detect the presence of Redonda phosphate as follows:—The substance

<sup>1</sup> Cf. Vol. I., p. 698.

<sup>2</sup> Landw. Versuchs-Stat., 1888, 35, 8.

<sup>3</sup> No. 100, Amandus Kahl, Hamburg.

<sup>4</sup> Mitteil. d. d. L. Ges., 1890-91, p. 131.

is shaken with cold sodium hydroxide solution, filtered, the filtrate just acidified with hydrochloric acid, and then a slight excess of ammonia added; it is said that 5 per cent. of Redonda phosphate will give rise to a bulky gelatinous precipitate of aluminium phosphate.

To recognise the presence of phosphorite meal as an adulterant, Böttcher<sup>1</sup> recommends the following test for the presence of fluorine:—Ten to fifteen grams of the slag are placed in a beaker about 10 cm. high and 5 to 6 cm. wide, 15 c.c. of concentrated sulphuric acid poured on, the mixture stirred with a glass rod, and the beaker quickly covered with a clock-glass carrying a drop of water on its under side. If a white, snow-like border is formed round the drop, it may be concluded with certainty that a mineral phosphate has been added. The clock-glass is removed after five to ten minutes, and it can then generally be distinctly seen whether it has been attacked by the hydrofluoric acid. Additions of 10 per cent. of raw phosphate can be thus detected.

## 6. PERUVIAN GUANO, CHINCHA ISLANDS GUANO, ETC.

### A. RAW PERUVIAN GUANO

1. *Moisture*.—This cannot be estimated in Peruvian guano in the ordinary way, since ammonia compounds would volatilise along with the water at 110°. It is, therefore, necessary to estimate the amount of ammonia volatilised, so that the true percentage of moisture may be calculated from the total loss in weight on drying. For this purpose 2 g. of the sample are weighed into a porcelain boat, which is then placed in the middle of a glass tube resting in a drying oven. One end of the tube is attached to a calcium chloride tube, the other to a Will and Varrentrapp receiver containing 100 c.c. of standard sulphuric acid. The oven is heated to 110°, and a current of dry, ammonia-free air is slowly sucked through the apparatus by means of an aspirator. After one hour's heating the apparatus is disconnected, the boat allowed to cool in a desiccator, and weighed; this gives the total loss in weight. Titration of the sulphuric acid in the receiver gives the amount of ammonia volatilised, which, subtracted from the total loss, gives the true percentage of moisture.

2. *Phosphoric Acid*.—This occurs in raw Peruvian guano in three different forms, viz., soluble in water, soluble in citrate solution, and insoluble.

Phosphoric acid soluble in water is estimated as in the case of superphosphates (p. 422).

Phosphoric acid soluble in citrate solution is estimated by Petermann's method (p. 400).

The insoluble or total phosphoric acid is determined by treating

<sup>1</sup> *Chem. Zeit.*, 1894, 18, 565.

10 g. of substance exactly as in the case of phosphatic guanos (p. 421), either with aqua regia, or with a mixture of nitric and sulphuric acids, and estimating the phosphoric acid by the citrate, molybdate, or Lorenz method.

3. *Nitrogen*.—Nitrogen also occurs in Peruvian guano in three different forms, viz., as organic nitrogen, combined as ammonia, and combined as nitric acid.

The total nitrogen is estimated in 1 g. of substance by Jodlbaur's or by Förster's method (*cf.* pp. 378 and 379).

The nitrogen combined as ammonia is liberated by distillation with ignited magnesia containing as little carbon dioxide as possible. Fifty c.c. (= 1 g. substance) of the aqueous extract obtained in estimating the phosphoric acid soluble in water are diluted with 150 c.c. of water, 3 g. of ignited magnesia added, and 100 c.c. of the liquid distilled off (*cf.* p. 380).

To estimate the nitrogen combined as nitric acid, 50 c.c. (= 1 g. substance) of the aqueous extract obtained in estimating phosphoric acid soluble in water are placed in the distillation flask of the Kjeldahl apparatus, 120 c.c. of water, 5 g. of reduced iron, about 5 g. of well-washed, nitrogen-free, zinc dust, and lastly, 80 c.c. of sodium hydroxide solution of sp. gr. 1.28 added, and the flask connected to the distillation apparatus, 20 c.c. of standard sulphuric acid being placed in the receiver. The flask is allowed to stand for from one to two hours, with frequent shaking, about 100 c.c. of liquid are distilled off, and the distillate titrated in the usual way. This estimation gives the nitrogen combined as ammonia and that present as nitric acid; the former being known, the latter is calculated by difference. The nitrogen combined as nitrate can also be estimated by the Schlösing-Grandeau-Wagner method (*cf.* p. 381).

The percentage of organic nitrogen is obtained by subtracting that combined as ammonia and as nitric acid from the total nitrogen.

4. *Potassium*.—Ten grams of substance are incinerated, the ash dissolved in dilute hydrochloric acid, and the solution diluted to 500 c.c.; 100 c.c. of this solution are then used for the estimation, as described on p. 410.

5. *Ash*.—Five grams of substance are incinerated in a platinum dish at the lowest possible temperature, and the ash weighed when cold.

6. *Examination as to Purity*.—The name "Peruvian Guano" is frequently applied to commercial manures which are artificially prepared mixtures of superphosphate, ammonium sulphate, Chili saltpetre, etc.

The importation of Peruvian guano into England has decreased largely of late years, and it is the exception to find it misdescribed. The term "Guano" is, however, often wrongly applied to mixtures and



to other materials, such as residues from extract of meat residues, but usually some qualifying word is used, such as "Meat guano," "Fish guano," etc.

An examination of Peruvian guano as to its genuineness is therefore very desirable. For this purpose the oxalic acid is first estimated. In genuine Peruvian guano it is present, and rises, up to 18 per cent., with the content of nitrogen. The quantitative estimation of the total oxalic acid is carried out as follows:<sup>1</sup>—Five grams of substance are boiled with 20 g. of sodium carbonate and about 20 c.c. of water in a 500 c.c. flask; when cold, the solution is diluted to the mark and filtered. Fifty or one hundred c.c. of the filtrate are just acidified with acetic acid, and the boiling solution precipitated with calcium acetate solution. The precipitated calcium oxalate is then treated in the usual way.

The presence of uric acid also serves as a test for the genuineness of Peruvian guano. This is tested for qualitatively by pouring dilute nitric acid on to a small quantity (1 to 2 g.) of the sample, and carefully evaporating to dryness. A yellow or yellowish red residue, changed to a fine purple by a trace of ammonia, indicates the presence of uric acid (murexide reaction). The addition of potassium or sodium hydroxide to the residue turns it reddish blue. The best method for the quantitative determination of uric acid is that of A. Stutzer and A. Karlowa.<sup>2</sup>

## B. DISSOLVED PERUVIAN GUANO

Only the percentages of phosphoric acid soluble in water and of the total nitrogen are usually estimated in this form of guano.

1. *Phosphoric Acid soluble in Water* is determined as in the case of superphosphates (p. 422).

2. *Total Nitrogen* is determined as in Peruvian guano (p. 429).

### 7. FISH GUANO, MEAT-MEAL, DRIED BLOOD, LEATHER AND HORN WASTE, POUDRETTE, WOOLLEN WASTE, SHODDY, ETC.

1. *Moisture*.—Five grams of substance are dried in the oven at 100° till the weight is constant.

2. *Phosphoric Acid*.—Ten grams of substance are boiled for half an hour in a 500 c.c. flask, either with 50 c.c. of aqua regia, or with a mixture of nitric and sulphuric acids, as described on p. 421; the solution is diluted with hot water, cooled, diluted to the mark, filtered, and 50 c.c. of the filtrate used to estimate the phosphoric acid either by the citrate, molybdate, or Lorenz method.

<sup>1</sup> Fresenius, *Quantitative Analysis*, translated by C. E. Groves, vol. ii., p. 586.

<sup>2</sup> *Chem. Zeit.*, 1896, 20, 721.

3. *Nitrogen*.—One gram of substance is decomposed either by Kjeldahl's or by Gunning's method (p. 377). If the substance is difficult to break up, so that 1 g. does not give a good average sample, 3 to 5 g. are weighed out, decomposed by 50 to 60 c.c. of sulphuric acid in presence of 2 to 3 g. of mercury, and the solution, when cold, washed into a 300 or 500 c.c. graduated flask, cooled, diluted to the mark, shaken vigorously, and then 100 c.c. distilled in the usual way.

4. *Ash and Sand* are determined as in the case of phosphatic guanos.

## 8. BONE-MEAL

### A. RAW AND STEAMED BONE-MEAL, BOILED BONES

1. *Moisture*.—Five grams of substance are dried in the oven at 100° till the weight is constant.

2. *Phosphoric Acid*.—Ten grams of substance are decomposed and treated exactly as in the case of fish guano, dried flesh, etc. (*cf.* No. 7, p. 430).

3. *Nitrogen* is estimated in 1 g. of substance either by Kjeldahl's or Gunning's method (p. 377).

4. *Ash, Organic Matter, and Sand*.—The following determinations must be made in order to judge whether a bone-meal has been manufactured solely from bones:—Five grams of substance are slowly incinerated in a platinum crucible or small platinum dish, the ash weighed when cold, thoroughly moistened with ammonium carbonate solution, dried at 160° to 180°, and weighed again. The residue thus obtained is called the "ignition residue." It is then boiled in a beaker with 20 c.c. of hydrochloric acid and a little water for half an hour, until everything has dissolved except the sandy portions of the sample and traces of unburnt carbon. The insoluble residue is collected on a filter, washed with boiling water, ignited, and weighed. After deducting the weight of the filter ash, the amount found is calculated as sand. Up to 9 per cent. of sand is admissible; a higher percentage than this proves adulteration.

Although sold in England upon a guarantee of phosphate and nitrogen, there is no fixed standard for the percentage of sand. The "ignition residue" minus the sand gives the amount of bone-ash.

The organic matter is given by the difference:  $100 - (\text{water} + \text{sand} + \text{bone-ash})$ .

Inferior phosphorite, rich in ferric oxide, is sometimes used to adulterate bone-meal. To detect this, Lorenz<sup>1</sup> recommends the following method:—Thirty grams of the bone-meal are treated with 10 to 15 c.c. of dilute sulphuric acid (1:1) in a beaker, stirred

<sup>1</sup> *Centralblatt für Agrikulture*, 1889, p. 89.

round with a glass rod, and quickly covered by a clock-glass with a drop of water on its under side. The presence of fluorine in the substance will give rise to the formation of a distinct white border round the drop; the border gradually increases in breadth and shows a delicate snow-like structure, which conclusively proves the presence of mineral phosphates.

Calcium sulphate is often added for the purpose of combining with ammonia formed from bones which have decomposed during storing. Bone-meal only contains a small quantity of sulphuric acid, so that the addition of calcium sulphate can be detected by the presence of much sulphuric acid.

The addition of sawdust is most easily detected by sulphuric acid, or microscopically; the acid colours sawdust black, while the organic constituents of bones are not coloured.

Brazil-nut dust is also used as an adulterant; it may very easily be detected by the microscope.

5. *Skin and Horn Constituents*.—Ten grams of the original bone-meal are placed in a glass cylinder of about 120 c.c. capacity, and vigorously and repeatedly agitated with about 100 c.c. of chloroform; after standing for a short time the horn-meal, etc., collects on the top, and may be conveniently removed by means of a small spoon and transferred to a dry filter without disturbing the bone-meal which collects at the bottom of the cylinder. The whole is then stirred up again, allowed to stand, and skimmed until horn-meal no longer collects on the surface of the chloroform. The filter and contents are washed with ether, dried at  $90^{\circ}$  to  $100^{\circ}$ , and weighed. The whole of the dried horn-meal is then used for a Kjeldahl nitrogen estimation.

6. *Carbon Dioxide* is estimated as in mineral phosphates (p. 420).

7. *Fat*.—To decide whether the bone-meal has been manufactured from bones which have or have not been deprived of fatty matter, it suffices to estimate the percentage of fat in the meal. For this purpose 5 g. of the finely powdered substance are dried in the oven at  $110^{\circ}$  till the weight is constant, then mixed with 10 g. of washed and ignited sand, and extracted with ether in the usual way.

8. *Fineness*.—This factor must also be considered in judging the value of bone-meal as a manure. It is determined as follows:—One hundred grams of the meal are separated into four portions of different degrees of fineness by means of three sieves. Stohmann has proposed the use of the following sieves: No. I., with 1089 meshes per square centimetre; No. II., with 484; No. III., with 256; that portion of the meal which remains on sieve No. III. is designated as meal No. IV.



## B. DISSOLVED BONES

1. *Moisture*.—Ten grams of substance are dried for three hours in the drying oven at 100°.

2. *Phosphoric Acid soluble in Water*.—As in superphosphates (p. 422).

3. *Total Phosphoric Acid*.—As in raw and steamed bone-meals (p. 431).

4. *Nitrogen*.—One gram of substance is decomposed either by Kjeldahl's or Gunning's method (pp. 375 and 377).

In so-called partially dissolved bone-meals, phosphoric acid soluble in citrate is generally guaranteed, as well as that soluble in water, and also the total phosphoric acid; the former is determined by Petermann's method (p. 400).

## 9. PHOSPHATIC GYPSUM

1. *Moisture*.—Five grams of substance are dried in the oven at 110°.

2. *Total Phosphoric Acid*.—As in the case of guano phosphates (p. 421).

3. *Phosphoric Acid soluble in Water*.—As in superphosphates (p. 422).

4. *Free Phosphoric Acid*.—Ten grams of the dried substance are shaken in the shaking machine for half an hour with 500 c.c. of absolute alcohol or ether, and the solution filtered immediately. Fifty c.c. of the filtrate (= 1 g. substance) are transferred to an Erlenmeyer flask, the alcohol evaporated off, the acid residue taken up with about 50 c.c. of water, and the phosphoric acid precipitated by magnesia mixture, filtered, ignited, and weighed in the usual way.

5. *Sulphuric Acid and Sand*.—Five grams of substance are placed in a 500 c.c. flask, treated with 15 c.c. of concentrated hydrochloric acid and about 400 c.c. of water, and warmed on the water-bath at about 50° for from four to six hours; the solution is allowed to cool, diluted to the mark, and filtered. One hundred c.c. of the filtrate are used to estimate the sulphuric acid by precipitation with barium chloride. The undissolved residue is thoroughly washed with boiling water, the filter dried and incinerated, and the residue, after deducting the filter ash, reckoned as sand.

## 10. GYPSUM

1. *Moisture*.—Five grams of the finely powdered substance are gently ignited over a small flame in a porcelain or platinum crucible for a quarter of an hour; the percentage of water is calculated from the loss in weight.

2. *Sulphuric Acid and Sand*.—As in phosphatic gypsum.

3. *Lime, Magnesia, etc.*—One hundred c.c. of the solution prepared for the estimation of sulphuric acid are heated in a beaker, ammonia

carefully added till just alkaline to litmus paper, the solution boiled to remove the ammonia,<sup>1</sup> and filtered. The slight residue is thoroughly washed on the filter with boiling water, dried, incinerated, ignited, and weighed; this, after deducting the filter ash, is calculated as  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ .

The filtrate, freed from iron, is heated to boiling, excess of ammonium oxalate, and then a little ammonia, added, and the beaker allowed to stand for twelve hours in a warm place. The clear supernatant liquid is carefully poured through a filter, the precipitate washed several times with hot water by decantation, transferred to the filter, dried, and ignited, finally for ten minutes on the blowpipe or in a Rössler furnace, and weighed as calcium oxide.<sup>2</sup>

To estimate the magnesia, the filtrate from the calcium oxalate precipitate is evaporated to about 100 c.c., excess of ammonia and sodium phosphate solution added, allowed to stand for twelve hours, and the precipitate of magnesium ammonium phosphate treated as in the estimation of phosphoric acid<sup>3</sup> (p. 391).

The amount of magnesia in the precipitate is obtained by multiplying the weight found by the factor 0.3623, from which the percentage of magnesia can be calculated.

## 11. NITRATES

### A. SODIUM NITRATE<sup>4</sup> (CHILI SALTPETRE)

1. *Moisture*.—Five grams of the sample are finely powdered and carefully heated over a small flame in a platinum crucible till the nitrate just fuses, and weighed, after cooling in the desiccator. The heating is repeated at the same temperature till no further loss takes place.

2. *Nitrogen*.—The nitrogen in sodium nitrate is determined by the zinc-iron method (p. 383) or by a similar direct method. The indirect method (by difference) is not admissible.<sup>5</sup>

3. *Sand*.—Ten grams of the finely powdered substance are dissolved in hot water, the solution filtered into a 500 c.c. flask, the filter washed with hot water, incinerated, and the residue weighed as sand. This residue may include matter other than sand.

4. *Chlorine, Sulphuric Acid, Lime, Magnesia, Sodium, and Potassium*.—The filtered solution obtained under (3) is cooled, diluted to 500 c.c., and well mixed. Fifty c.c. serve for the estimation of the chlorine, either by titration or by precipitation with silver nitrate, and a further 50 c.c. are precipitated hot with barium chloride to estimate the sulphuric acid. The calcium is precipitated in the usual way by

<sup>1</sup> Cf. Vol. I., pp. 273 and 610.

<sup>2</sup> Cf. Vol. I., p. 405.

<sup>3</sup> Cf. also Vol. I., p. 406.

<sup>4</sup> Cf. Vol. I., p. 306.

<sup>5</sup> Cf. *Landw. Versuchs-Stat.*, 1893, 42, 130, 134.

ammonium oxalate, and the magnesium by sodium phosphate. The sodium is either estimated by difference, or it may be determined as follows:—Fifty c.c. of the above solution are just acidified with sulphuric acid, evaporated to dryness, and the residue ignited till its weight is constant. The weight of calcium and magnesium sulphates are subtracted, and the remainder, representing sodium sulphate, multiplied by the factor 0.4364, gives the amount of sodium as oxide ( $\text{Na}_2\text{O}$ ). If potash be present, it is estimated in the usual way and subtracted.

5. *Perchlorate*.<sup>1</sup>—Deleterious effects on crops have frequently been observed after dressing with sodium nitrate, the cause of which was attributed by B. Sjollesma<sup>2</sup> to sodium perchlorate. Recent observations on the marked sensitiveness of rye to perchlorate have proved that 1 per cent. of perchlorate in Chili saltpetre, an amount harmless to other field produce, must be considered dangerous as regards rye, under certain circumstances, a still smaller percentage (*e.g.*, 0.5 per cent.) of perchlorate may do damage to rye.

For the estimation of perchlorate, Loges<sup>3</sup> recommends the ignition of the nitrate with a little alkali hydroxide or carbonate; this gives the total chlorine originally combined as chloride, chlorate, and perchlorate. The chlorine originally present as chloride is then estimated in the aqueous solution of the nitrate, and the percentage of chlorate plus perchlorate calculated by difference.

If chlorate is to be estimated separately, 5 g. of the nitrate are gently boiled for half an hour with 10 g. of washed, chlorine-free, zinc dust, and 150 c.c. of 1 per cent. acetic acid solution. The chlorine originally combined as chloride plus chlorate is thus obtained in the filtrate as chloride and estimated.

Förster<sup>4</sup> mixes 10 g. of the nitrate with 10 g. of chlorine-free anhydrous sodium carbonate, and ignites the mixture till the melt is quite liquid and no longer swells up, an operation which occupies at most ten minutes. The melt is dissolved in an excess of nitric acid, and the total chlorine estimated either gravimetrically or volumetrically by Volhard's method<sup>5</sup> (titration with potassium thiocyanate).

Blattner and Brasseur<sup>6</sup> recommend the following method:—Five or ten grams of the dry, finely powdered nitrate are mixed with 8 or 15 g. of pure quicklime, slaked lime, or calcium carbonate, and the mixture heated in a large platinum or porcelain crucible by a Bunsen flame for about fifteen minutes. When cold, the mass is dissolved in dilute nitric acid, and the total chlorine determined by one of the usual methods. The best results are obtained when slaked lime is used.

<sup>1</sup> Cf. Vol. I., p. 319, and this Vol., p. 484.

<sup>2</sup> *Chem. Zeit.*, 1896, 19, 1002.

<sup>3</sup> *Landw. Versuchs-Stat.*, 1898, 50, 39.

<sup>4</sup> *Chem. Zeit.*, 1898, 22, 357.

<sup>5</sup> Cf. Vol. I., p. 123.

<sup>6</sup> *Chem. Zeit.*, 1898, 22, 589.



C. Gilbert<sup>1</sup> has proposed various other methods (ignition with pyrolusite, etc.); a further method has also been described by Selkmann.<sup>2</sup>

Sjollema<sup>3</sup> gives the following as a qualitative test for perchlorate:—One hundred grams of the nitrate are dissolved in 500 c.c. of water, and an aliquot portion of the solution treated with an excess of moist silver oxide and filtered. A portion of the filtrate is then evaporated to dryness and ignited, the residue taken up with hot water, acidified with nitric acid, and tested for chloride with silver nitrate solution.

Fresenius and Bayerlein<sup>4</sup> recommend M. von Breukeleveen's method, conducted as follows, as a qualitative test:—About 10 to 20 g. of a good average sample of the nitrate are dissolved in an equal quantity of water with the aid of heat, and the solution filtered hot. Four to six drops of the clear filtrate are placed on an object-glass and a few tiny crystals of rubidium chloride added, which dissolve rapidly. The liquid is then coloured a distinct wine-red by mixing with it a little potassium permanganate solution. The object-glass is then placed over a small flame so that the liquid begins to evaporate, and this evaporation is continued until the crystalline crusts which form at the edge are about 4 mm. wide; on removing the object-glass from the flame, tiny isolated crystals form in the still liquid portion of the preparation. At this point the heating is interrupted, the glass placed under the microscope, and the growth of the crystals in the interior of the preparation watched. Well-developed, colourless crystals of rubidium nitrate will form, accompanied, if perchlorate be present, by individual crystals of rubidium perchlorate; the latter are coloured intense red-violet and appear in the form of obliquely truncated, prismatic needles, frequently forming stellate groups.

#### B. POTASSIUM NITRATE<sup>5</sup> (SALTPETRE)

1. *Moisture, Nitrogen, Chlorine, Sulphuric Acid, Lime, Magnesia, and Sand* are all estimated as in the case of sodium nitrate.

2. *Potassium*.—Ten grams of the finely powdered substance are dissolved in 500 c.c. of water, 50 c.c. of the solution repeatedly evaporated to dryness with hydrochloric acid in order to convert the nitrate into chloride, the residue then taken up with water, the sulphuric acid precipitated by barium chloride, the filtrate treated with ammonia and ammonium carbonate, etc., and the potassium estimated, after ignition, in the usual way, as potassium platinichloride (*cf.* p. 410).

#### C. CALCIUM NITRATE

The nitrogen is estimated as in sodium nitrate.

<sup>1</sup> *Methoden zur Bestimmung des Perchlorats im Chili-salpeter*, Tübingen, 1899.

<sup>2</sup> *Z. angew. Chem.*, 1898, **11**, 101.

<sup>4</sup> *Z. anal. Chem.*, 1898, **37**, 501.

<sup>3</sup> *Chem. Zeit.*, 1897, **21**, 44.

<sup>5</sup> *Cf.* Vol. I., p. 538, and this Vol., p. 481.

12. SULPHATE OF AMMONIA<sup>1</sup>

1. *Moisture*.—Five grams of the finely powdered substance are dried in the oven at 110° till the weight is constant.

2. *Nitrogen*.—Ten or twenty grams of substance are dissolved in 500 or 1000 c.c. of water, 25 c.c. of the solution (=0.5 g. substance) are transferred to the distillation flask of a Kjeldahl apparatus, 3 g. of burnt magnesia (free from carbon dioxide) and 150 c.c. of water added, and the ammonia distilled off, and collected in sulphuric acid in the usual way.

3. *Tests for purity*.—Ammonium sulphate must be tested for thiocyanates by adding hydrochloric acid and ferric chloride; the presence of ammonium thiocyanate gives rise to a blood-red coloration.

Cyanogen compounds are detected by adding sodium or potassium hydroxide, then ferrous sulphate and ferric chloride, and acidifying with hydrochloric acid; a blue coloration indicates cyanide.

## 13. CALCIUM CYANAMIDE (NITROLIM)

One gram of the sample is taken for the estimation of nitrogen, either by Kjeldahl's or by Gunning's method; two hours' heating with phosphor-sulphuric acid suffices for the decomposition, even if the residual solution remains black and is not clear.

## 14. POTASSIUM SALTS

1. *Moisture*.—Five grams of the finely powdered substance are carefully heated over a small flame for a short time in a covered platinum crucible, and then gently ignited for about ten minutes, until no further diminution in weight takes place.

2. *Potassium*.—To estimate the soluble potassium salts, the substance is passed through a 1 mm. sieve, and 10 g. of the prepared sample boiled for a quarter of an hour with 400 c.c. of water; when cold, the solution is diluted to 500 c.c., and an aliquot part (100 c.c.) precipitated hot by barium chloride to separate the sulphuric acid; the filtrate is then treated with ammonia and ammonium carbonate, etc., as described on p. 410,<sup>2</sup> or by the perchlorate method.

Kainite and potassium chloride contain only a little sulphate, together with the chloride; in these the potassium may be estimated by the shortened method (p. 411).

3. *Lime and Magnesia*.—Ten grams of substance are dissolved in dilute hydrochloric acid in a 500 c.c. flask, the solution diluted to the mark, and 100 c.c. treated with ammonia till strongly alkaline; the solution is heated, and an excess of ammonium oxalate added to

<sup>1</sup> Cf. also the section on "Coal-Gas and Ammonia," this Vol., p. 746.

<sup>2</sup> Cf. also Vol. I., p. 408.

precipitate the calcium. The precipitate is filtered, after standing for twelve hours, ignited, finally on the blowpipe, and weighed as calcium oxide.

Sodium phosphate and ammonia are added to the filtrate to precipitate the magnesia; the solution is left to stand for twelve hours, filtered, and the precipitate ignited and weighed as magnesium pyrophosphate.

4. *Chlorine, Sulphuric Acid, and Sand* are determined in the usual way (*cf.* p. 434).

## 15. MIXED MANURES

(*Ammonium superphosphates, Potassium superphosphates, Potassium-ammonium superphosphates, Nitrate superphosphates.*)

1. *Moisture*.—Ten grams of substance are dried for three hours in the oven at  $100^{\circ}$ , and the percentage of moisture calculated from the loss in weight.

2. *Phosphoric Acid*.—This falls under the three heads:—Phosphoric acid soluble in water, reverted or citrate-soluble phosphate, and total phosphate; each is estimated as in pure superphosphates (p. 422).

3. *Nitrogen*.—(a) *The Nitrogen present exclusively in the form of Ammonia*.—The estimation of ammoniacal nitrogen in ammonium superphosphates or other mixed manures, in which nitrogen is guaranteed in that form, is effected by distilling an aliquot portion of the solution, corresponding to 1 g. substance, with magnesia (*cf.* p. 380). The solution is prepared by shaking 20 g. of substance in 1 litre of water, as in the case of superphosphates (p. 422). The nitrogen thus determined is termed “ammoniacal nitrogen.”

(b) *The Nitrogen present as Nitric Acid*.—This is estimated by the Schlösing-Grandeau-Wagner method (p. 381), or by one of the reduction methods (p. 382 *et seq.*).

(c) *The Nitrogen combined both as Ammonia and as Nitrate*.—If the two forms of nitrogen are not to be estimated separately, one of the reduction methods is used. The nitrate is first reduced, and the ammonia distilled off in the usual way; this gives the ammoniacal plus nitrate nitrogen. If the ammoniacal nitrogen is then estimated by distillation with ignited magnesia, the difference will give the percentage of nitrate nitrogen.

(d) *The Nitrogen combined as Ammonia, as Nitrate, and as Organic Nitrogen*.—The total nitrogen is estimated by Jodlbaur's or by Förster's method (pp. 378 and 379). If it be desired to separately determine the three forms of nitrogen, that combined as ammonia and as nitrate must be estimated by the method given above; the amount of organic nitrogen is given by the difference:—total nitrogen minus (ammoniacal plus nitrate nitrogen).



4. *Potassium*.—To estimate the soluble potassium salts, 10 g. of the finely powdered substance are boiled for a quarter of an hour with 400 c.c. of water; when cold, the solution is made up to 500 c.c. and filtered. One hundred c.c. of the filtrate are precipitated hot with barium chloride to remove the sulphuric acid, the filtrate treated with ammonia and ammonium carbonate, and the analysis completed in the usual way (*cf.* p. 410).

## 16. LIME MANURES

The following substances are included under this heading :—

A.—1. Burnt Lime, either in pieces or ground.

2. Burnt slaked Lime.

3. Burnt or burnt and slaked grey Lime (burnt lime rich in magnesia).

B.—4. Lime-Marl and Alumina-Marl.

5. Dolomitic Marl.

C.—6. Mixtures of A. and B. in varying proportions.

7. Residual Lime, by-products of chemical manufacture.

The important constituents to be estimated in lime manures are the lime and magnesia, which are present in a basic form, *i.e.*, as oxide, hydroxide, or carbonate, not that combined with other acids, such as calcium sulphate and silicate or magnesium silicate.

*Sampling*.—In the case of burnt lime, a large number of pieces are selected from the heap, broken into pieces of the size of a hazel nut, and a representative sample of 500 g. selected and placed in a dry, well-stoppered bottle. Ground manures are sampled as in the case of other manures; since lime manures contain free lime and accordingly tend to absorb moisture and carbon dioxide during transit, the samples for analysis should be taken after the removal of the upper layer of the consignment, or, if packed in sacks, from the middle of the sack. In all cases the samples should be packed in air-tight bottles, not in boxes.

The sample thus obtained is carefully powdered for analysis so as to pass through a 1 mm. sieve and a portion of the sieved material then passed through the sieve used for basic slag (p. 427).

*Method of Analysis*.—The estimation of the basic constituents in lime manures of classes (A. 1) and (A. 2) of known origin, and which contain not more than 5 per cent. of magnesia, is carried out as follows:—0.25 g. of the sample is shaken up with 200 c.c. of warm water, treated with 20 to 25 c.c. of standardised sulphuric acid of about  $N/5$  concentration, the evolved carbon dioxide removed by boiling, and the excess of acid titrated back with sodium or barium hydroxide, using phenolphthalein as indicator. The result is calculated as calcium oxide, without regard to the magnesia present.

In the case of grey limes (A. 3), an estimation of magnesia is also made, and the result used for the calculation of the content of basic lime.

Moisture is estimated in the case of lime manures containing free lime or calcium hydroxide, by igniting 1 to 2 g. of the sample in a tube, and absorbing the water given off in a weighed calcium chloride tube.<sup>1</sup> Carbon dioxide is estimated either by loss or volumetrically.

Lime- and alumina-marls (B. 4) of known origin, and which do not contain more than 5 per cent. of magnesia, are valued by estimating the carbon dioxide and calculating it to calcium carbonate, or the above method of analysis can be applied. In the case of dolomitic marls, the magnesia is also determined and calculated to carbonate.

Mixtures of lime manures (C. 6) are tested as above for basic constituents, moisture, and carbon dioxide; if they contain much magnesia, this constituent is estimated separately.

Residual lime must be tested for constituents injurious to plants.

The following method for the estimation of the basic constituents has been proposed by O. Förster.<sup>2</sup> Hydrochloric acid is used in place of sulphuric acid, as the results with the latter reagent are not quite reliable. The method is also applicable to the analysis of soils. The sample is prepared by the method generally adopted for manures, and 4 to 5 g. in the case of burnt lime, and 8 to 10 g. in the case of carbonates, are taken for the analysis. This is weighed into a 400 or 500 c.c. graduated flask, treated with 200 or 250 c.c. of  $N/1$  hydrochloric acid, and the whole shaken repeatedly in the cold for several hours; or, the mixture is warmed for half an hour on the water-bath. The solution is then made up to the mark, so that the contained acid becomes diluted to half-normal strength. The solution is filtered, and 100 c.c. of the filtrate transferred to a 200 c.c. graduated flask, titrated with  $N/2$  sodium hydroxide, using phenolphthalein as indicator till the colour-change takes place, 1 to 2 c.c. of  $N/2$  hydrochloric acid added, heated to boiling for a few minutes until the carbon dioxide is completely removed, and the excess of acid titrated back with the alkali. This titration can be satisfactorily effected if the samples are very pure and there is only a slight separation, if any, of sesquioxides, but as a rule it is advisable to dilute the solution with water, free from carbon dioxide, to 200 c.c., filter, and to take 100 c.c. of the filtrate for the final titration.

The incomplete neutralisation of the hydrochloric acid solution previous to filtration is to be recommended, as the greater portion of the sesquioxides are thereby separated and can be removed by filtration,

<sup>1</sup> Cf. J. König, *Untersuchung landwirthschaftlich u. gewerblich wichtiger Stoffe*, 2nd edition, 1898, p. 107.

<sup>2</sup> *Landw. Versuchs-Stat.*, 1908, 69, 235; *J. Chem. Soc. Abstr.*, 1908, 94, 1072.

so that they do not interfere with the recognition of the colour-change in the subsequent titration; an excess of acid is, however, essential in order to avoid the precipitation of calcium hydroxide and its removal by filtration. One hundred c.c. of the solution as prepared above corresponds to 100 c.c. of  $N/2$  acid. Accordingly, for the calculation of the result, the total c.c. of  $N/2$  alkali used are subtracted from the 100 c.c. of  $N/2$  acid, and the difference multiplied by 0.014.

*Example.*—(i.) *Lime.*—Volume of solution taken 100 c.c. = 1 g. of substance = 100 c.c.  $N/2$  acid. Volume of  $N/2$  alkali used 33 c.c.;  $100 - 33 = 67$  c.c.  $N/2$  acid = 0.938 g. CaO = 93.8 per cent.

(ii.) *Calcium carbonate.*—Volume of solution taken 100 c.c. = 2 g. of substance = 100 c.c.  $N/2$  acid. Volume of  $N/2$  alkali used 36 c.c.;  $100 - 36 = 64$  c.c.  $N/2$  acid = 0.896 g. CaO = 44.8 per cent.

Förster is of the opinion that normal calcium silicates should be included amongst the basic-forming constituents of lime manures, although they are not so included by the regulations adopted by the Union of Agricultural Laboratories in Germany.

### 17. SULPHUR

The degree of fineness of sulphur is determined by means of Chancel's sulphurimeter as described in Vol. I., pp. 265-6.<sup>1</sup>

## III.—APPENDIX

### DIRECTIONS FOR THE EXAMINATION OF MANUFACTURED PRODUCTS, AND OF THE RAW MATERIALS OF MANURE MANUFACTURE CONCERNED IN INTERNATIONAL TRADE

*(Agreed upon by the International Committee for the Analysis of Artificial Manures and Feeding Stuffs at the Fifth International Congress for Applied Chemistry, Berlin, 1903.)*

#### SAMPLING

1. Irregular samples are to be returned by the analyst, or the fact is to be notified on the certificate of analysis.

2. Official samples must be taken during unloading at the last railway station or port, either in presence of witnesses belonging to both parties, or by a sworn expert, the following instructions being observed.

3. In the case of manufactured products, a sample is to be taken from every tenth bag by means of a sampler; in the case of cargo in bulk, from at least ten different places.

<sup>1</sup> Details of the regulations adopted by the Union of Agricultural Laboratories in Germany for the examination of Sulphur are described in the 3rd German edition, Vol. III., pp. 71-73.



4. In the case of a cargo of raw material, every fiftieth bucket or barrowful unloaded (*i.e.*, 2 per cent. of the material) is to be thrown on to the sample heap; when this has been through the first crushing and has been reduced at least to the size of hazel nuts, a sample is taken for the estimation of moisture; for the analysis, a sample is taken from the completely crushed material, as in the case of manufactured products.

5. The samples must be loosely put into strong, clean, perfectly dry, glass vessels; each sample should weigh about 300 g.

6. At least three samples are to be taken in each case and hermetically sealed with the seals of the samplers.

7. The label must be fastened on with the same seals and bear the signature of the sampler.

8. The samples are to be stored in a cool, dark, dry place.

9. Substances of uneven composition must be sufficiently powdered and mixed before filling the sample bottles.

### Preparation of the Samples

1. Dry samples of phosphates or other artificial manures should be passed through a sieve and then mixed.

2. The preparation of moist manures, which cannot be thus treated, must be confined to careful and thorough mixing by hand.

3. As proof of the identity of raw phosphates and bone black, the percentage of moisture is determined.

4. Where the percentage of moisture changes during pulverisation it must be determined in both the fine and the coarse material, and the result of the analysis must be recalculated on the basis of the moisture in the original, coarse material.

## METHODS OF ANALYSIS

### 1. Moisture.

Ten grams of substance are used and dried at  $100^{\circ}$  till of constant weight; if the substance contain gypsum it must be dried for three hours.

In the case of potash salts the determinations of the Syndicate of Potash Works of Leopoldshall-Stassfurt are valid.

### 2. Insoluble Matter.

Ten grams of substance are used :—

(a) When dissolved in mineral acids the silica is rendered insoluble and the residue ignited.

(b) When dissolved in water the residue is dried at  $100^{\circ}$  till of constant weight.

### 3. Phosphoric Acid.

#### *Preparation of Solutions.*

1. To estimate phosphoric acid soluble in water, 20 g. of substance are shaken in a litre flask with about 800 c.c. of water for thirty minutes, and then filled to the mark. Solutions of so-called double superphosphates must be boiled with nitric acid before precipitation of the phosphoric acid in order to convert any pyrophosphoric into orthophosphoric acid. Ten c.c. of concentrated nitric acid are used for every 25 c.c. of superphosphate solution.

*N.B.*—If phosphoric acid soluble in citrate solution is to be determined in the superphosphate, Petermann's method must be applied.

2. To estimate total  $P_2O_5$ , 5 g. of substance are boiled with aqua regia (see table, p. 444), or with 20 c.c. of nitric acid and 50 g. of concentrated sulphuric acid for thirty minutes, and diluted to 250 c.c.

3. Basic slag: Phosphoric acid.

If the basic slag appear to contain coarser portions, it is sifted through a 2 mm. sieve, and the agglomerated portions remaining on the sieve are distributed over it by slight pressure. The portion which passes through the sieve is used for the estimation of phosphoric acid, and the coarser portions are taken into account in calculating the result.

(a) Phosphoric Acid soluble in Citric Acid.—Five grams of substance are weighed into a 500 c.c. flask containing 5 c.c. of alcohol (to prevent the substance sticking to the bottom), shaken with 2 per cent. of citric acid solution (*cf.* table, p. 444) at  $17^{\circ}.5$  for half an hour in a rotation apparatus making thirty to forty revolutions per minute.

(b) Total Phosphoric Acid.—Ten grams of substance are placed in a 500 c.c. flask, thoroughly moistened with about 5 c.c. of water, and then boiled for thirty minutes with 50 c.c. of concentrated sulphuric acid, the flask being frequently shaken round, and finally filled to the mark.

If it be desired to estimate "Fine Meal," a sieve of 0.17 mm. mesh-width is used. (No. 100, Amandus Kahl, Hamburg).

#### *Analysis of Solutions.*

1. Molybdate method, as given by Fresenius and P. Wagner.

2. Citrate method.

3. Free acid.

(a) Total amount of free acids. The aqueous solution (No. 1) is titrated with sodium hydroxide, using methyl orange as indicator.

(b) Free phosphoric acid is estimated gravimetrically in the alcoholic solution.

The method employed must be stated.

#### 4. Ferric Oxide and Alumina.

These must be estimated by E. Glaser's method, including the improvements made by R. Jones, or, where the estimation of alumina is concerned, by H. Lasne's method.<sup>1</sup>

The method used must be stated.

#### 5. Nitrogen.

*Nitrogen combined as Nitrate.*—Direct methods only are admissible.

(a) The reduction methods of Böttcher,<sup>2</sup> Ulsch, Devarda, and Kjeldahl-Jodlbaur.

(b) The gas-analytical methods of Lunge and Schlösing-Grandeau.

2. *Ammoniacal Nitrogen.*—The estimation must be conducted by distillation with magnesia; in the case of ammonium superphosphates the solution described under No. 3, 1 (p. 443) must be used.

3. *Total Nitrogen.*—In presence of nitrates this must be determined by the Kjeldahl-Jodlbaur method.

4. *Organic Nitrogen.*—If nitrates and ammonium salts are absent, Kjeldahl's method or Will and Varrentrapp's method of ignition with soda lime is used.

#### 6. Potassium.

This must be estimated with chloro-platinic acid or with perchloric acid. The method used must be stated.

#### 7. Calcium and Magnesium.

For lime and calcareous marl Tacke's<sup>3</sup> volumetric method may be used; or the usual gravimetric methods may be applied. The method used must be stated.

Table for a Uniform Nomenclature of Chemical Reagents and Apparatus.

No.	Designation.	Spec. Grav. and Composition.
1	Sulphuric acid . . . . .	1.40 = 50 per cent. H <sub>2</sub> SO <sub>4</sub> .
2	Conc. sulphuric acid . . . . .	1.84 = 100 "
3	Nitric acid . . . . .	1.20 = 32 " HNO <sub>3</sub> .
4	Conc. nitric acid . . . . .	1.52 = 100 "
5	Hydrochloric acid . . . . .	1.12 = 24 " HCl.
6	Conc. hydrochloric acid . . . . .	1.20 = 39 "
7	Ammonia . . . . .	0.96 = 10 " NH <sub>3</sub> .
8	Conc. ammonia . . . . .	0.91 = 25 " "
9	Aqua regia . . . . .	1.12 = 3 " hydrochloric acid.
		1.20 = 1 " nitric acid.
10	Citric acid . . . . .	20 g. pure crystallised acid per 1 litre.
11	Rotation apparatus . . . . .	30 to 40 revolutions per 1 minute.
12	Shaking machine . . . . .	150 revolutions per 1 minute.

<sup>1</sup> *Bull. Soc. Chim.*, 1896 [4], 15, pp. 118-128, 146-157, 237-248.

<sup>2</sup> Formerly called Kühn's method; cf. *Landw. Versuchs-Stat.*, 1892, 41, 165, 370.

<sup>3</sup> *Landw. Versuchs-Stat.*, 3, p. 76, and 4, p. 8.



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## FEEDING STUFFS

By F. BARNSTEIN, Ph.D., Möckern. English translation revised  
by ALFRED SMETHAM.

### I.—EXAMINATION OF CONCENTRATED FOOD STUFFS

**Sampling.**—Oilcake is sampled by taking several whole cakes from different parts of the bag; these are broken up into pieces about the size of a walnut, thoroughly mixed, and a sample for analysis then taken.

In the case of seeds, meal, pollard, bran, and such like, packed in sacks, sampling is best effected by laying the sack on its side and introducing the sampling auger into different layers of the contents. It is also permissible to empty a number of sacks and to mix their contents on a clean floor; samples are then taken from different parts of the heap with a shovel or auger (*cf.* Vol. I., p. 13).

In the case of a cargo of raw material, every fiftieth bucket or barrowful unloaded (*i.e.*, 2 per cent. of the material) is thrown on to the sample heap, thoroughly crushed, and reduced at least to the size of hazel nuts, and a sample taken.

From 100 to 200 g. of the average sample thus obtained are ground in a suitable mill till the meal will pass through a 1 mm. sieve. In the case of some feeding stuffs, particularly palm-nut meal, further milling is desirable.

The following estimations are of special importance in the chemical examination of feeding stuffs, *viz.* :—Water, fat, albuminoids, ash, crude fibre, and soluble carbohydrates.

**Moisture.**—This is estimated with sufficient accuracy for commercial purposes as follows :—About 5 g. of the meal are heated for three hours in a water-jacketed drying-oven at 95° to 100°, in small beakers about 6 cm. high and 3 cm. in diameter; the beakers are placed in a desiccator to cool, and the loss in weight determined.

When this method is used the temperature must not be raised above 95° to 100°, nor must the drying be prolonged appreciably beyond three hours, especially when the dried substance is to be used for the estimation of fat; failure to observe these precautions may entail oxidation of the fat (*e.g.*, in the case of poppy-seed cake or linseed cake) or its volatilisation (*e.g.*, grains and linseed cake).

If a very accurate estimation of moisture be required, the feeding stuff is heated at  $100^{\circ}$  to  $102^{\circ}$  in a current of dry hydrogen or coal gas until the loss of weight is constant.

**Fat.**—The substance, previously dried as above, is placed in a paper cylinder (Schleicher and Schüll), the cylinder closed by a wad of fat-free cotton wool, and placed in a Soxhlet extractor, provided with sufficient ether, and heated by a water-bath till the ether boils vigorously. The extraction takes, at the most, twelve hours. The ether is then distilled off, the residue dried in a water-jacketed drying-oven for one to two hours, and weighed when cold. If the determination of moisture is not required the air-dry substance may be weighed in a boat, transferred immediately to the cylinder, and then dried for three hours.

According to the decisions of the International Congress for Applied Chemistry (Berlin 1903), only ether free from alcohol and water may be used for the extraction of fat.

It is to be noted that the ethereal extract designated as "fat" may contain, besides neutral fats and fatty acids, other non-fatty substances such as colouring matter, wax-like compounds, organic acids, hydrocarbons, etc.

C. Beger<sup>1</sup> has shown that in the case of some feeding stuffs, such as gluten meal, malt culms, brewer's grains, poppy-seed cake, distillery meal, and meat meal, the fat cannot be completely extracted by direct extraction with ether. He therefore proposed to determine the fat in these feeding stuffs, particularly for scientific purposes, by Dormeyer's method. This consists in allowing 3 to 5 g. of the substance to digest for twenty-four hours at  $37^{\circ}$  to  $40^{\circ}$  with 1 g. of pepsin (Merck), 480 c.c. of water, and 20 c.c. of 25 per cent. hydrochloric acid; the insoluble portion is filtered off, thoroughly washed, dried, and extracted with ether. The filtrate is repeatedly shaken up with ether, and the ether residue added to that extracted from the insoluble portion. The pepsin solution is then filtered with the help of a pump through a Buchner funnel provided with filter paper and fine asbestos.

Loges<sup>2</sup> suggests, as a quick method giving approximate results, that 5 g. finely pulverised and dried material be shaken for half an hour with 100 c.c. of water-free ether in a Wagner rotating apparatus; the ether is evaporated off from 50 c.c. of the filtrate and the residue weighed.

In judging the freshness of oilcake and oilcake meal it is desirable to know the percentage of free fatty acids in the same. In most cases it is sufficient to dissolve the ether extract, obtained in the determination of fat, in ether, and to estimate the fatty acids in this solution by titration with *N*/10 alcoholic sodium hydroxide, using phenolphthalein as indicator. The solution should be titrated until permanently red

<sup>1</sup> *Chem. Zeit.*, 1902, 26, 112.

<sup>2</sup> *Landw. Versuchs-Stat.*, 1906, 64, 28.



(1 c.c. *N*/10 sodium hydroxide = 0.0284 g. oleic acid). Aqueous sodium hydroxide can also be used if the ether solution of the fat is mixed with an equal quantity of alcohol.

Free fatty acids may partially volatilise during the drying of the feeding stuff and ethereal extract, or oxygen may be taken up and oxidation products of the fat may be formed. Hence, the undried material must be used for more accurate determinations of the fatty acids. To this end, 10 g. of the substance are digested with 100 c.c. of ether for three hours, or, if a shaking machine be used, for a half to one hour; 25 c.c. of the ethereal extract are then titrated as above.

This last method for the estimation of fatty acids is particularly adapted to palm-nut and cocoa-nut cake or meal and to all feeding stuffs which have undergone lengthy storage, as it gives both the volatile and non-volatile free fatty acids.

**Total Albuminoids.**—The percentage of nitrogen in the feeding stuff is determined by Kjeldahl's or Gunning-Atterberg's method, as described in the section "Manures," p. 375). In the case of oilcake-meals, 1 g. of substance is decomposed, in the case of bran, grains and distillery meal, about 1.5 g. For meat-meal, gluten-meal, and other feeding stuffs very rich in nitrogen, 2 to 3 g. of substance are decomposed by about 30 to 40 c.c. of sulphuric acid in presence of about 1 g. of mercury; the product is diluted with water, allowed to cool, diluted to 500 c.c., and the nitrogen in 100 c.c. estimated. Some feeding stuffs, such as distillery refuse, grains, bran, etc., are apt to froth considerably when decomposed by sulphuric acid containing phosphoric acid. In such cases it is advisable to place a small quantity of paraffin wax, a pea-sized piece is ample, in the decomposition flask before starting to heat.

The amount of nitrogen found is multiplied by 6.25 and the product is designated "total albuminoids." The use of the factor 6.25 is founded on the assumption that vegetable albumin contains 16 per cent. of nitrogen. It has been found, however, that the percentage of nitrogen is higher than this (between 16.38 and 18.73 per cent.), and accordingly various factors have been proposed so that the product should more accurately express the percentage of albuminoids; none of these, however, have yet come into general use.<sup>1</sup>

The nitrogenous substances designated as "total albuminoids" consist chiefly of albumin, amido-compounds, alkaloids, etc. In investigating feeding stuffs the estimation of true albuminoids, which is of special importance, is carried out according to the following directions of Stutzer:—One hundred c.c. of water are poured on to 1 to 2 g. of the sample in a beaker, the liquid heated to

<sup>1</sup> According to the Board of Agriculture and Fisheries Regulations, the factor 6.25 is imperative.

boiling, or, when the material contains starch-flour, heated in a boiling water-bath for ten minutes, then treated with 0.3 to 0.4 g. of cupric hydroxide, suspended in water, filtered when cold, and the residue on the filter thoroughly washed with water. This residue, together with the filter paper, is decomposed by Kjeldahl's method by sulphuric acid containing phosphoric acid in presence of about 1 g. of mercury, and the ammonia then distilled off. The small amount of nitrogen in the filter paper may generally be neglected.<sup>1</sup>

If the substance contain alkaloids, the following treatment must precede that with cupric hydroxide. It is digested for ten minutes on the water-bath with 100 c.c. of absolute alcohol just acidified by the addition of a few drops of concentrated acetic acid; the undissolved substance is allowed to settle and the alcoholic liquid carefully poured off through a filter, allowing little or none of the sediment to pass on to the filter. One hundred c.c. of water are then poured on to the residue, and further treated as described above. When the feeding stuffs are rich in alkaline phosphates (*e.g.*, oil-cake meal, bran), 1 c.c. of alum solution (1:10) is added to the hot liquid before adding the cupric hydroxide. The potassium is thus combined as sulphate, and so rendered incapable of dissolving albumin and preventing its precipitation.

To avoid the addition of alum solution and the tedious preparation of the cupric hydroxide mixture, Barnstein has worked out a method for the estimation of albuminoids based on that of O. Kellner. This method differs from that of Stutzer in that the cupric hydroxide is not added as such, but is precipitated in the liquid containing the albuminoids. To the solution, prepared by boiling or digesting the substance with hot water, 25 c.c. of copper sulphate solution are added, containing 60 g. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  per litre. Then 25 c.c. of dilute sodium hydroxide solution (12.5:1000) are slowly added while the solution is stirred, the precipitate allowed to settle, and further treated as in Stutzer's method. The concentrations of the copper sulphate and sodium hydroxide solutions are chosen so that the whole of the copper is not precipitated by the alkali, while the precipitate produced contains as much effective cupric hydroxide as is used in Stutzer's method.

One advantage of this method is that the precipitate generally

<sup>1</sup> The cupric hydroxide is prepared according to the following directions:—One hundred grams of copper sulphate are dissolved in 5 litres of water, 2.5 g. of glycerine, and then dilute sodium hydroxide added, till the solution is alkaline. The precipitate of cupric hydroxide is filtered off, then suspended again in water containing 5 g. of glycerine per litre, and completely freed from alkali by repeated washings by decantation and on the filter. The residue is finally rubbed up with water containing 10 per cent. of glycerine, and diluted with the same solution till the mixture can be sucked up into a pipette. The content of copper is then estimated by evaporating a measured volume of the solution to dryness and igniting the residue. It is best to dilute the solution so that 20 or 25 c.c. contain 0.3 to 0.4 g. of cupric hydroxide.

settles more rapidly and completely than is the case in Stutzer's method. The results obtained by the two methods agree in the case of most feeding stuffs. Vegetable products, however, containing alkaloids or other nitrogenous compounds of basic character (amides, etc.), give a precipitate containing a little more nitrogen when treated by the latter method than when that of Stutzer is used; this difference never exceeds 0.2 per cent. of nitrogen.<sup>1</sup>

In the case of feeding stuffs containing starch flour the washing out of the cupric hydroxide precipitate is very tedious. Kellner has accordingly proposed the following method for the estimation of the non-albuminoid nitrogen:—Ten grams of the sample are treated with 250 c.c. of 40 per cent. alcohol slightly acidified with acetic acid, in a 500 c.c. flask, and digested for one hour in a boiling water-bath; the flask is then filled up to the mark with 40 per cent. alcohol, the contents shaken, filtered, 100 c.c. of the filtrate mixed with 25 c.c. of copper sulphate solution and 25 c.c. of sodium hydroxide solution of the concentration given above, the whole made up to 200 c.c., thoroughly mixed and filtered; 100 c.c. of the filtrate (= 1.0 g. substance) are then carefully evaporated with a little sulphuric acid, with the addition of about 1 g. of mercury. The nitrogen is then estimated as usual and calculated to non-albuminoid nitrogen by multiplying by the factor 6.25. The result obtained, deducted from the "Total albuminoids" found, gives the "True albuminoids" present.

**Digestible Albuminoids.**—The method introduced by Stutzer and improved by Kühn and Kellner, consists in digestion with acid gastric juice.

The digestion liquid is prepared as follows:—The mucous membranes of ten pigs' stomachs are cut with scissors into fine strips, 49 litres of water and 1 litre of 12½ per cent. hydrochloric acid poured over them, and left to digest, with frequent shaking, for two to three days in a cool place. The liquid is then poured off through a small flannel bag, and finally filtered through a double folded filter. As a preservative, 0.5 per cent. of chloroform is added to the digestion liquid, which is stored in closed vessels in a dark place.

Digestion is conducted by pouring 500 c.c. of the digestion-liquid on to 2 g. of the substance under examination, and warming to 37° to 38° on a water-bath or in an incubator. After about twelve hours, 10 c.c. of 12.5 per cent. hydrochloric acid are added, and the same addition repeated after twenty-four and thirty-six hours, so that at the end of this time the liquid contains approximately 1 per cent. of hydrochloric acid. After the lapse of a further twelve hours the digestion liquid is filtered from the undissolved substance, the latter washed with water, alcohol, and ether, and together with the filter paper, decomposed with 30 c.c.

<sup>1</sup> Cf. Landw. Versuchs-Stat., 1900, 54, 327.



of sulphuric acid by Kjeldahl's method; the percentage of undigested nitrogen is thus estimated. A blank experiment should be made. As an alternative, half the hydrochloric acid to be used may be added at the beginning of digestion and the other half after the lapse of twenty-four hours. The liquid must be frequently stirred during digestion, and the vessel covered to prevent evaporation.

K. Wedemeyer<sup>1</sup> has devised a method in which commercial pepsin is substituted for gastric juice. The pepsin must conform to the test prescribed by the German Pharmacopœia III., viz., "An egg is placed for ten minutes in boiling water and then allowed to cool; when cold, the white is rubbed through a sieve suitable for the preparation of a coarse powder. Ten grams of the white of egg thus broken up are mixed with 100 c.c. of warm water at 50° and ten drops of 25 per cent. hydrochloric acid; 0.1 g. of pepsin is then added. The mixture is kept for an hour at 45° with frequent shaking; at the end of this time the white of egg must have completely disappeared, with the exception of some slight whitish yellow membranes." If the pepsin does not dissolve to a perfectly clear solution in 0.5 per cent. hydrochloric acid, the solution must be filtered.

Wedemeyer gives the following directions for the digestion:—Two grams of the feeding stuff are placed in a beaker and treated with 490 c.c. of a clear solution, containing 1 g. of pepsin and 10 c.c. of 25 per cent. hydrochloric acid. The beaker is covered with a glass plate and digested at 37° to 40° for forty-eight hours, with frequent stirring. Ten c.c. of 25 per cent. hydrochloric acid are added after the lapse of twenty-four hours, thus bringing up the amount of acid to 1 per cent. When digestion is complete the undissolved substance is collected on a filter, and washed with warm water until the filtrate no longer contains chloride; it is then washed with alcohol, and finally very thoroughly with ether. The nitrogen in the undissolved substance and filter is then estimated. A blank experiment should be made.

Some foodstuffs, such as the husks of umbelliferous seeds (*e.g.*, caraway, anise, coriander, fennel), must be digested for a longer time (eighty-four hours) with gastric juice or pepsin solution.<sup>2</sup>

**Crude Fibre.**—This is estimated by Weender's method as described by Henneberg and Stohmann.

From 3 to 4 g. of substance (corresponding to about 3 g. of the dried substance) are boiled for half an hour with 50 c.c. of 5 per cent. sulphuric acid and 150 c.c. of water in a specially adapted porcelain dish which is provided with a mark indicating the level of 200 c.c. of liquid; the water evaporated during the boiling is replaced. The solid matter is then allowed to settle, the supernatant liquid poured

<sup>1</sup> Landw. Versuchs-Stat., 1899, 52, 375.

<sup>2</sup> Cf. Landw. Versuchs-Stat., 1894, 44, 188.

into a beaker, and the residue boiled for a quarter of an hour with distilled water; after settling, the liquid is poured into the same beaker, and the operation repeated. The liquid thus collected in the beaker is allowed to stand for a short time, so that any fibrous particles which have been carried off may settle; the greater part of the liquid is then syphoned off without disturbing the sediment; what remains, together with the contents of the porcelain dish, is poured through a filter. The residue is rapidly washed on the filter by pouring hot water on to it, and then washed back into the dish with 200 c.c. of 1.25 per cent. potassium hydroxide; it is then boiled again for half an hour, then twice with water for a quarter of an hour, finally collected on a weighed filter, very thoroughly washed successively with water, hot alcohol and ether, dried, and weighed immediately in a closed weighing-bottle.

Experiments by Uhlitzsch have shown that before Weender's method can be applied to the determination of crude fibre in the waste from umbelliferous seeds, it is absolutely necessary that the latter should be thoroughly freed from fat.

Another and much more expeditious method of determining crude fibre is that described by Gabriel,<sup>1</sup> in which the methods of Lange and of Hönig are combined as follows:—Two grams of substance are heated in an Erlenmeyer flask to 180° with 60 c.c. of a glycerine solution of potassium hydroxide (33 g. potassium hydroxide dissolved in 1 litre of glycerine); the flask is allowed to cool to 140°, and its contents poured into a dish containing 200 c.c. of boiling water. After stirring round and allowing the residue to settle, the liquid is drawn off by a syphon; a piece of linen must be stretched over the end of the latter. The precipitate is then twice boiled up with 200 c.c. of water, 5 c.c. of 25 per cent. hydrochloric acid being added the second time, collected on a weighed filter, thoroughly washed with water, alcohol and ether, dried, and weighed.

Crude fibre prepared either by Weender's or by Gabriel's method, is not pure cellulose, but contains nitrogenous constituents and ash, and also a certain amount of pentosans, which, in a more accurate estimation, would have to be separately determined and subtracted.

In the following method, due to König,<sup>2</sup> the crude fibre is obtained almost completely free from pentosans:—Three grams of air-dry substance (*i.e.*, containing 5 to 14 per cent. of water) are placed in a dry porcelain dish of 500 c.c. capacity, and mixed with 200 c.c. of glycerine, (sp. gr. 1.230) containing 20 g. of concentrated sulphuric acid per litre. The dish is placed in a digester and heated for exactly one hour at 137°, then allowed to cool to between 80° and 100°, taken out, its contents diluted with 200 to 250 c.c. of boiling water, and filtered hot through an asbestos filter on the pump. The residue on the filter is washed with

<sup>1</sup> *Z. physiolog. Chem.*, 1893, 16, 270.

<sup>2</sup> *Z. Unters. Nahr. u. Genussm.*, 1898, 1, 3.

300 to 400 c.c. of hot water, and finally with alcohol and ether; it is then transferred, together with the asbestos, to a platinum crucible, dried, and weighed. The crude fibre is then completely incinerated, and the crucible again weighed. The difference between the two weighings gives the amount of ash-free crude fibre.

The arrangement illustrated in Fig. 68 allows of several determinations being conducted simultaneously. The stand fits a digester about 25 cm. in height and 20 cm. interior diameter. If not prevented, the water condensing on the lid of the digester would drop into the upper dish and so vitiate the concentration of the glycerine; to obviate this the dish is covered with a slightly curved lid. The use of a digester is preferred, as more uniform results are obtained.

Rapid filtration is secured by the arrangement shown in Fig. 69,



FIG. 68.

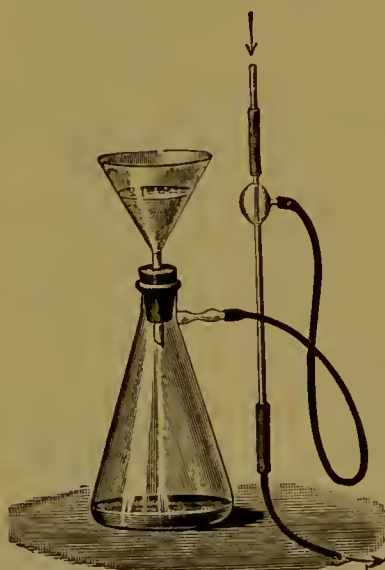


FIG. 69.

in which a porcelain plate with fairly wide perforations and of about 65 mm. diameter is placed in the funnel, covered with a circular piece of filter paper, and then with fine asbestos suspended in water; the asbestos is evenly distributed with the help of the pump in sufficient quantity to give a clear filtrate; a relatively thin layer of asbestos suffices for this purpose.

If a digester is not available, 3 g. of substance are placed in a flask of about 600 c.c. capacity, and heated to boiling on a reflux condenser with about 200 c.c. of glycerine-sulphuric acid for exactly one hour. The flask must be shaken round whenever the liquid threatens to froth. After boiling, the flask is allowed to cool to 80° or 100° and its contents treated as described above.

Fig. 70 represents the apparatus used by König for four simultaneous determinations without the use of a digester. The small glass tube



passing through the stopper of the flask is connected to the condenser by rubber tubing in such a way that the flask can be conveniently shaken round.

König has, in addition, given details for the separation of pure cellulose from the residue obtained from the glycerine-sulphuric acid.<sup>1</sup> This estimation is carried out as follows:—A second sample of 3 g. of either air-dry substance or of products containing 5 to 14 per cent. of moisture is weighed out and treated as described above. The residue in the Gooch crucible is not dried, but is transferred to a beaker of 800

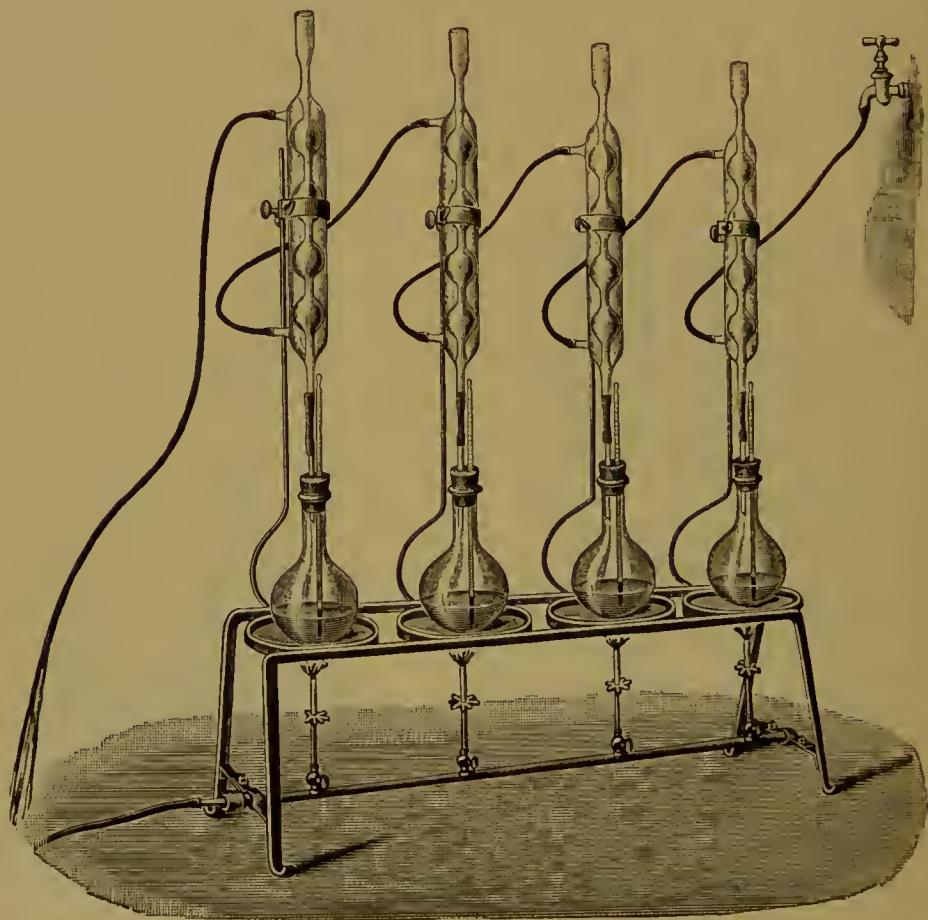


FIG. 70.

c.c. capacity, together with the asbestos filter, after the ether has been allowed to evaporate spontaneously; the beaker is covered with a glass plate, and 100 to 150 c.c. of chemically pure, 3 per cent. by weight hydrogen peroxide added, together with 10 c.c. of 24 per cent. ammonia, and the whole allowed to stand for twelve hours. Then 10 c.c. of 30 per cent. by weight of hydrogen peroxide are added, and this addition repeated, after the evolution of oxygen has ceased, until the crude fibre is quite white; 5 c.c. of 24 per cent. ammonia are added with the third or fifth addition of the peroxide. The residue is then warmed in the

<sup>1</sup> *Z. Unters. Nahr. u. Genussm.*, 1903, 6, 76.

water-bath for one to two hours, filtered through a second asbestos filter, and then treated as described above. The weight of crude fibre, less that of the cellulose, gives the weight of lignin present.

**Ash.**—Five to ten grams of the feeding stuff are heated in a platinum dish over a small flame until either completely burnt, or, as in the case of substances containing easily fusible salts, completely charred. In the latter case the charcoal is protected from further combustion by a coating of salt; it is, therefore, extracted with water, dried, and then completely burnt. The aqueous extract is washed back into the dish, evaporated on the water-bath, and the residue dried and weighed.

Difficultly combustible feeding stuffs are generally more easily incinerated if the flame is removed after charring and the dish allowed to cool. The finely divided charcoal then absorbs oxygen, and burns more easily when heated again. The size of the flame is increased towards the end of the process, until the ash is white.

Complete combustion is most easily attained by the use of a low temperature and free access to air. Too high a temperature should be avoided (Smetham).

The ash thus obtained (crude ash) contains the mineral ingredients of the plant, some carbon, often sand, and, in the case of those feeding stuffs which contain an organic acid combined with a base, a certain amount of carbonic acid.

The weight of pure ash, free from carbon, sand, and carbonic acid is obtained as follows:—The ash is washed with distilled water into a small Erlenmeyer flask, and the carbon dioxide first estimated as described on p. 420. The solution is then diluted with water, boiled for ten minutes with hydrochloric acid, the residue collected on a weighed filter and washed with hot water till the filtrate no longer contains chloride, and the residue dried and weighed as carbon plus sand. Finally, the filter and contents are incinerated, and the weight of sand thus obtained. Crude ash — (carbon + sand + carbon dioxide) = pure ash.

Hemp-seed waste, and the feeding stuffs prepared from barley, oats, and rice always contain a certain amount of silica as apart from sand in the ash. Such substances should be evaporated to dryness with hydrochloric acid before weighing the silica.

If it be required to determine the sand in these feeding stuffs the ash is boiled, as directed above, with hydrochloric acid, the insoluble residue washed and ignited, then boiled with concentrated sodium carbonate solution (100 parts of water to 25 parts of anhydrous sodium carbonate), the residue again filtered off, washed with hot water, ignited, and weighed as sand.

More accurate results are obtained by the method proposed by

F. Mach. Ten grams of the sample are boiled for four minutes with 200 c.c. of 5 per cent. sulphuric acid, the solution diluted to about 1000 c.c. in a beaker, and the bulk of the solution syphoned off, after allowing the insoluble matter to settle. The residue is then washed into a porcelain dish with 200 c.c. of a 25 per cent. sodium carbonate solution, boiled for half an hour, the evaporated water being replaced during this boiling, transferred to a beaker, diluted to a 1000 c.c., the liquid again syphoned off, and the residue filtered and washed. It is then further purified by boiling successively with hydrochloric acid and with water, filtered and washed, and the residual sand weighed.

The following method of estimating sand was suggested by Emmerling; it is frequently applied in making a preliminary test for sand, but gives only approximately accurate results. A long glass funnel of the form shown in Fig. 71 is connected by means of rubber tubing to a calibrated measuring tube, and filled nearly up to the base of the conical part with a concentrated solution of zinc sulphate (1 kg. of the crystallised salt to 725 g. of water). Water is carefully poured into the conical part of the funnel, then 20 g. of the feeding stuff placed in the same part and stirred round as long as grains of sand are seen to sink down in the zinc sulphate solution; finally, the zone of separation of the two layers is stirred up. As soon as the sand has settled in the measuring tube its level is read off (one division equals 0.2 g. or 1 per cent. of sand). Oil cake should be softened before the test by boiling it with water, since the sand does not separate from it so easily.



FIG. 71.

Loges uses chloroform in place of zinc sulphate for separating the sand.

*Total Constituents of Ash.*—If it be required to estimate all the constituents of the ash of the plant, the hydrochloric acid extract of the crude ash is used for the estimation of the bases. The silica is first separated by twice evaporating to dryness, the residue then taken up with water containing hydrochloric acid and a few drops of nitric acid, and the solution diluted to 500 c.c. Two hundred c.c. of this solution are treated with ammonia until it is only slightly acid, ammonium acetate solution then added, and warmed. The precipitated ferric phosphate is filtered off, ignited, and weighed; half the weight of the precipitate is taken as ferric oxide. The filtrate is slightly warmed, acetic acid added, and the calcium precipitated by ammonium oxalate. The filtrate from the calcium oxalate is treated with a little sodium phosphate, evaporated to about 100 c.c., excess of ammonia added, the precipitate filtered off after standing for twelve hours, and weighed as magnesium pyrophosphate.

For the estimation of the potassium, sodium, and sulphuric acid,



100 c.c. of the hydrochloric acid solution of the ash are treated with a hot solution of barium chloride, to separate the sulphuric acid. Ammonia and ammonium carbonate are added to the filtrate from the barium sulphate, the precipitate filtered off, the filtrate evaporated to dryness in a platinum dish, the ammonium salts driven off at as low a temperature as possible, the residue taken up with water, a little oxalic acid added, the solution again evaporated, and the residue carefully and continuously ignited until the free oxalic acid is driven off and the oxalates are converted into carbonates. The residue from this ignition is extracted with water, the solution again evaporated with oxalic acid, the residue ignited, and finally taken up with water, and the solution evaporated with a little hydrochloric acid. The residue of sodium and potassium chlorides is weighed, dissolved in water, the solution filtered if necessary, the potassium precipitated by chloroplatinic acid and estimated as described in the section on "Manures," p. 410.

To estimate the phosphoric acid, the solution of the ash is freed from silica, then repeatedly evaporated with nitric acid to remove chlorine, and the phosphoric acid estimated by the molybdate method (*cf.* p. 389).

For the determination of the chlorine, the ash is extracted with nitric acid, and the extract either precipitated with silver nitrate or titrated by Volhard's method.

To examine vegetable matter which has been damaged by waste water or by furnace smoke, for sulphuric acid, copper, lead, zinc, and arsenic, it is advisable to incinerate the material by adding it gradually to a fused mixture of 6 g. of pure potassium hydroxide and 3 g. of potassium nitrate. The melt is dissolved in hydrochloric acid, the solution freed from silica, and examined for substances injurious to plants by the usual methods of analysis.

**Nitrogen-free Extractive Matters.**—These are not, as a rule, estimated in feeding stuffs by direct analysis, but calculated by subtracting the sum of water, albuminoids, fat, ash, and crude fibre from 100; the difference is designated as "Nitrogen-free Extractive Matters," or more commonly as "Carbohydrates, etc."

The most important of the substances included under this head are sugars, starch, and dextrin. The plant contains in addition, gum, mucilage, organic acids, pectin, bitter principles, colouring matter, etc., and also, as B. Tollens has pointed out, pentosans.

**Sugar, Starch, and Dextrin.**—For the estimation of these substances, 5 to 20 g. of the sample are extracted three times with cold water and three times with 200 c.c. of hot water; substances containing starch are extracted six times with cold water only. The extraction must be completed in the shortest possible time (in summer within twenty-four

hours), as a precaution against decomposition of the extract by the formation of mould, or by fermentation.

The aqueous extract is filtered on the pump, and diluted to a definite volume (1000 to 1200 c.c.). To estimate dextrin, 200 to 500 c.c. are concentrated in a dish to about 20 c.c., and then gradually mixed with 200 c.c. of alcohol (95 per cent. by volume), with continuous stirring; the precipitate, which contains the dextrin, is allowed to settle, the alcoholic solution poured off through a filter, the residue in the dish thoroughly washed with 92 per cent. alcohol by repeatedly rubbing it up with a pestle, and the washings united to the first filtrate. The alcoholic solution is then evaporated to dryness, the residue dissolved in about 10 c.c. of hot water, again precipitated by 100 c.c. of alcohol, and washed as described above; the precipitates are similarly treated, after dissolving them in hot water and concentrating the solution to about 10 c.c.

The alcoholic filtrates contain the sugars, which are estimated as detailed below. The precipitates are dissolved in 200 c.c. of hot water, and three portions of the solution are boiled on a reflux condenser with 20 c.c. of hydrochloric acid (sp. gr. 1.125) for one, two, and three hours respectively. Each is then quickly cooled, sodium hydroxide added till neutral or only slightly acid, the solution diluted till it contains, at most, 1 per cent. of dextrose, and 25 c.c. taken for its estimation by the Meissl-Allihn gravimetric method, which is described in the Section on "Spirits," Vol. III. The highest of the three results thus obtained is regarded as the correct one; the amount of dextrin present is found by multiplying the amount of dextrose found by 0.90.

For the determination of the sugar in the alcoholic extract (if dextrin is absent, the original aqueous extract is used), the alcohol is evaporated off, and the residue dissolved in water; the amount of the latter must be so regulated that the solution does not, if possible, contain less than 0.245 g., but on no account more than 1 per cent. of sugar; the sugar is then estimated either volumetrically or gravimetrically. The appropriate methods, as well as that for the estimation of starch, are described in detail in other Sections ("Beer," "Spirits," etc., Vol. III.).

**Pentosans.**—As far as the analysis of feeding stuffs is concerned, these include all substances which give furfural on distillation with hydrochloric acid.

Appropriate methods of estimation have been described by B. Tollens.<sup>1</sup> Of these only the simplest, the phloroglucinol method, will be described; it is carried out as follows:—

Two to five grams of the substance under examination are placed in a flask of about 300 c.c. capacity, and distilled with 100 c.c. of hydro-

<sup>1</sup> Landw. Versuchs-Stat., 1893, 42, 381, 398; Z. Ver. Rübenzuckerind., 1894, 44, 460.

chloric acid (sp. gr. 1.06) over a bath of Rose's metal (one part each of lead, tin, and bismuth). Thirty c.c. of liquid are distilled off, and then replaced in the distillation flask by 30 c.c. of the same acid; 30 c.c. are again distilled off, and this operation is continued until the distillate amounts to nearly 400 c.c. Pure phloroglucinol, dissolved in a little hydrochloric acid (sp. gr. 1.06) is then added, to the extent of double the amount of furfurol expected, the solution diluted with the same acid to 400 c.c., stirred round, left to stand till the next day, filtered through a Gooch crucible fitted with asbestos, the precipitate washed with 150 c.c. of water at 15° to 20°, dried for four hours in a water-jacketed drying oven, and weighed.

Tollens calculates the amount of furfurol from the weight of the precipitate as follows: if the amount of the latter is small, he divides by 1.82; if large, by 1.93.

$$(\text{Furfurol} - 0.0104) \times 1.88 = \text{Pentosan } (\text{C}_5\text{H}_8\text{O}_4).$$

$$(\text{Furfurol} - 0.0104) \times 2.13 = \text{Pentose } (\text{C}_5\text{H}_{10}\text{O}_5).$$

E. Kröber has subjected the above method to critical examination, and has worked out a table which enables the amount of pentosans corresponding to the weight of phloroglucide found to be read off directly.<sup>1</sup>

**Mustard Oil.**—Potassium myronate frequently occurs in rape-seed cake, especially in that prepared from Indian seed. This forms poisonous mustard oil when in contact with water, under the influence of the enzyme myrosin, which is contained in the seed. It is, therefore, sometimes necessary to examine rape-seed cake with respect to the amount of mustard oil which may be formed in it. According to Förster, this may be effected as follows:—

Twenty-five grams of the cake meal are stirred up with 150 c.c. of water in a flask; if necessary, white mustard must be added. The flask is closed by a ground stopper, into which two glass tubes are fused; one conducts steam into the mixture, the other leads the vapours to a condenser, with which an air-tight joint is made. After standing for half an hour, steam is passed into the flask and the distillate collected in a receiver fitted with an air-tight connection to the condenser; in the receiver are placed 50 c.c. of alcoholic ammonia, with which the mustard oil combines to form allylthiourea, which is difficultly volatile.

When about 200 c.c. of liquid have distilled over, the condenser water is turned off, and alcohol vapour passed through the condenser tube until it is thoroughly washed. The contents of the receiver are well mixed, left to stand for twelve hours, transferred to a large beaker, and heated to boiling; 0.8 g. of freshly precipitated mercuric oxide are

<sup>1</sup> *J. für Landwirtschaft*, 1900, p. 357.



then added and the liquid kept boiling for a few minutes longer, bumping being prevented by continual stirring. The mercuric oxide is prepared by adding an excess of potassium hydroxide to 25 c.c. of 4 per cent. mercuric chloride solution, and heating to boiling; the precipitate and liquid are used together.

Twenty-five c.c. of 4 per cent. potassium cyanide solution are added before the liquid has completely cooled, to dissolve the excess of mercuric oxide and the dimercuric-ammonium hydroxide formed, and the liquid stirred round for a few minutes. The precipitated mercuric sulphide is collected on a weighed filter, washed with hot water, dried at  $100^{\circ}$  to  $110^{\circ}$ , and weighed. The weight of mercuric sulphide, multiplied by 0.4266, gives the amount of mustard oil formed.

The presence of mustard oil may be confirmed by gradually heating the meal with water in a stoppered bottle, when a strong odour of mustard oil is developed.

A. Schlicht has also worked out a method of estimating mustard oil. He states that the results given by Förster's method are too low. The difference, however, is too slight to influence any conclusions to be drawn from the analysis of the material.

**Hydrocyanic Acid.**—Within recent years certain beans, such as Moon beans, Java beans, and Kratok beans, have come into the market, which evolve hydrocyanic acid in the intestinal canal, and consequently exert a poisonous action. Linseed also gives rise to the same acid.

For the detection of hydrocyanic acid, Guignard<sup>1</sup> recommends the isopurpuric acid reaction, a red coloration formed on addition of alkali and picric acid.<sup>2</sup> This reagent is prepared in the form of a test paper by dipping filter paper into a 1 per cent. aqueous solution of picric acid, and then, after drying, in a 10 per cent. solution of sodium carbonate. To carry out the test, a few grams of the powdered beans are placed in a flask in which a strip of the test paper is suspended, moistened with water, and the flask closed. With 2 g. of a substance containing 0.015 g. of hydrocyanic acid per 100 g., the coloration is formed after standing for a few hours in the cold; the coloration remains for a considerable time if kept in the dark.

The hydrocyanic acid produced from a considerable quantity of the ground beans can be estimated by distillation of the infusion with steam; the hydrocyanic acid in the distillate is then determined colorimetrically, either as Prussian blue or as thiocyanate.

## II.—EXAMINATION OF GREEN FODDER, HAY, AND STRAW

It is best to sample these feeding stuffs during unloading. A handful is taken from every second fork, the sample cut fine by a straw-

<sup>1</sup> *Comptes rend.*, 1906, 142, 545.

<sup>2</sup> Cf. A. C. Chapman, *Analyst*, 1910, 35, 469.

cutter, very carefully mixed, then spread out, and a portion taken as the sample for analysis; care must be taken, especially in the case of hay, to include the finest portions lying at the bottom.

The green fodder, hay, or straw must be dried before it is milled for analysis. This is done by heating a large weighed quantity (up to 2000 g.) to about  $80^{\circ}$  for some time, until the mass is uniformly dry; if digestibility is to be determined, the temperature must not exceed  $50^{\circ}$ . The material is then left to lie in the air for several days, or, in the case of feeding stuffs with coarse stalks, for several weeks; the air-dry substance is weighed again, and kept in well-closed vessels ready to be broken up fine.

The analysis of this dried material is conducted according to the methods described above for Concentrated Food Stuffs (I.); the results obtained must of course be recalculated to the original condition of the sample.

### III.—EXAMINATION OF POTATOES, TURNIPS, AND TURNIP LEAVES

The sampling and the preparation for analysis of both potatoes and of turnips is the same. A suitable quantity is washed free from sand and dirt, carefully dried with a cloth, and weighed. The roots are then cut up, the slices strung on to a string, and dried as described under II.

Dried turnip leaves have recently been introduced as feeding stuffs. These contain varying amounts of oxalic acid, which is determined as follows (Grandeau):—Ten grams of the sample are ground to a paste with dilute sulphuric acid (1 : 5), powdered pumice added so as to form a granulated product, and the whole extracted with ether in a suitable apparatus. The ether extract, from which the oxalic acid may in part crystallise out, is shaken with water, so as to obtain an aqueous solution of the acid, this solution filtered, neutralised with ammonia, then acidified with acetic acid, and the oxalic acid precipitated by calcium acetate.

The analytical methods used for the examination of these products are in part described under I., and in part in other sections (*cf.* "Starch," Vol. III.).

### IV.—EXAMINATION OF ACID FODDERS, DISTILLERY REFUSE, GRAINS, ETC.

Part of the material is used in its original state, or after extraction with water, for the estimation of free acid by titration. The rest is dried, milled, and examined in the usual way.

In the case of distillery refuse, the weight of a litre is determined, and the results of analysis calculated in terms of litres or hectolitres and of kilograms.

Kellner's researches have shown that acid fodder loses an appreciable amount of nitrogen if it is dried without special precautions; the cut mass should be moistened with hydrochloric acid before drying.

#### V.—EXAMINATION OF MOLASSES FEEDING STUFFS

It is generally required to estimate the percentage either of molasses or of absorbent. Either Schmöger's or Neubauer's method may be used for the purpose; the former is preferable when the percentage of fat is also required; it is carried out as follows:—<sup>1</sup>

The feeding stuff is dried for about three hours at 80°, and ground in a suitable mill. Five grams are placed on a filter attached to the pump, or in a large Gooch crucible, and about 100 c.c. of cold water are allowed to trickle through the mass, whereby all soluble matter is thoroughly washed out; the residue is dried in a water-jacketed drying oven, and weighed when cold. The amount of the air-dry absorbent is calculated from the result, taking into account the solubility of the absorbent and the mean amount of moisture which it contains. The following table of the more common absorbents shows the amount of dry absorbent soluble in 100 c.c. of water:—

Animal meal . . . . .	14.5	Malt culms . . . . .	36.5
Barley meal . . . . .	83.2	Meat meal (Liebig) . . . . .	2.3
Blood meal . . . . .	9.5	Millet meal . . . . .	5.2
Brewers' grains . . . . .	5.9	Millet chaff . . . . .	2.8
Cocoanut cake . . . . .	27.3	Oat shudes . . . . .	2.5
Coffee husks . . . . .	1.1	Palmnut cake . . . . .	9.8
Cotton seed husks . . . . .	13.1	Pea pods . . . . .	2.9
Cotton seed meal . . . . .	18.6	Peat fibre . . . . .	0.5
Distillery grains . . . . .	4.1	Potato pulp . . . . .	12.5
Distillery refuse, dried . . . . .	9.3	Rice chaff . . . . .	2.2
Gluten meal . . . . .	4.8	Rice meal . . . . .	11.4
Groundnut cake . . . . .	21.4	Rye bran (fine) . . . . .	21.5
Groundnut husks . . . . .	7.2	Rye straw (chaff) . . . . .	4.8
Hemp seed cake . . . . .	8.5	Sunflower seed cake . . . . .	17.4
Maize germ cake . . . . .	7.2	Turnip parings . . . . .	9.8
Maize gluten waste . . . . .	1.4	Wheat bran (fine) . . . . .	17.5
Maize, ground . . . . .	5.4	Wheat bran (coarse) . . . . .	15.3

Neubauer's method of determining the percentage of molasses in molasses feeding stuffs consists in estimating the moisture, and determining the specific gravity of an aqueous extract; the required figure is then calculated from the following formula:—<sup>2</sup>

$$Mx = M \frac{w(s-1) - aT}{M(1-T) - s}.$$

M is the specific gravity of dry molasses, = 1.69;

<sup>1</sup> *Landw. Versuchs-Stat.*, 1902, 57, 27.

<sup>2</sup> Cf. *Landw. Versuchs-Stat.*, 1898, 50, 421.



$T^1$ , the weight of matter soluble in water, contained in 1 g. of the dry absorbent; it is calculated, with certain assumptions, from the specific gravity of the solution.

$a$ , the weight of dry feeding stuff used for the experiment.

$w$ , the weight of water contained in a certain molasses solution.

$s$ , the specific gravity at  $15^\circ$  of an aqueous extract prepared from the feeding stuff.

$x$ , the required volume of dry molasses in the feeding stuff, expressed in cubic centimetres;  $Mx$  is thus the required weight of molasses.

$M$  and  $T$  are mean values, deduced from a large number of determinations; the quantities  $w$ ,  $s$ , and  $a$  must be directly determined for each investigation.

The following example illustrates the application of the method to the determination of the percentage of molasses in a sample of sugar feed prepared from grains.

Moisture is estimated by drying 3 g. at  $100^\circ$  till of constant weight. Result:—16.00 per cent. of water, corresponding to 84.00 per cent. of the dry feeding stuff ( $a$ ).

Ten grams of substance are placed in a tared flask of about 200 c.c. capacity, 100 c.c. of water added, the whole weighed, the flask well corked, and allowed to stand for two hours at the ordinary temperature with frequent shaking. At the end of this time some of the liquid is filtered into a Reischauer pyknometer, the temperature adjusted to  $15^\circ$ , and the apparatus filled to the mark; the specific gravity of the filtrate is then determined by weighing. All the required data are thus known.

It is assumed that:—

$$M = 1.69, \text{ and } T = 0.025$$

Weight of flask + water + 10 g. substance . . . . .	= 149.790 g.
Tare of flask . . . . .	= 39.763 g.
Weight of water added . . . . .	= 100.027 g.
Weight of water in the substance . . . . .	= 1.600 g.
Total weight of water ( $w$ ) . . . . .	= 101.627 g.
Weight of dry feeding stuff used . . . . .	= 8.400 g.
Specific gravity of the solution . . . . .	= 1.0190 g.

Using these values, the formula gives:—

$$Mx = 1.69 \times \frac{101.627 (1.0190 - 1) - 8.4 \times 0.025}{1.69 (1 - 0.025) - 1.0190} = 4.626$$

The sugar feed thus contains 46.26 per cent. of dry molasses.

<sup>1</sup>  $T$  is calculated from the formula  $\frac{W}{A}(S - 1)$ . The symbols  $W$ ,  $A$ ,  $S$  have the same meaning for the absorbent as the symbols  $w$ ,  $a$ ,  $s$  have for the feeding stuff, and are determined in the same way.

The dry substance in the feeding stuff amounts to 84.00 per cent.  
 Amount of dry molasses found . . . 46.26 - -  
 Hence the amount of dry absorbent is . . . 37.74 per cent.

The average moisture in air-dry brewers' grains amounts to 10 per cent.; hence the sugar feed contains  $37.74 + 4.19 =$  about 41.9 per cent. brewers' grains and  $100 - 41.9 = 58.1$  per cent. molasses.

The mean values of  $T$  which have been found for the various absorbents, and the product,  $M(1 - T)$ , are given in the following table:—

Absorbent.	T.	M(1 - T).
Animal meal . . . . .	0.064	1.5818
Barley meal . . . . .	0.055	1.5971
Blood meal . . . . .	0.042	1.6190
Brewers' grains . . . . .	0.025	1.6478
Cocoanut meal . . . . .	0.122	1.4838
Cotton-seed husks . . . . .	0.058	1.5920
Cotton-seed meal . . . . .	0.082	1.5514
Distillery grains . . . . .	0.018	1.6596
Dried distillery refuse . . . . .	0.028	1.6427
Gluten meal . . . . .	0.021	1.6545
Groundnut husks . . . . .	0.026	1.6461
Malt culms . . . . .	0.153	1.4314
Maize germ cake meal . . . . .	0.027	1.6444
Maize gluten waste . . . . .	0.006	1.6799
Meat meal . . . . .	0.010	1.6731
Millet chaff . . . . .	0.022	1.6528
Millet meal . . . . .	0.031	1.6376
Oat shudes . . . . .	0.011	1.6714
Palmnut meal . . . . .	0.039	1.6241
Pea pods . . . . .	0.013	1.6680
Peat fibre . . . . .	0.007	1.6782
Potato pulp . . . . .	0.055	1.5871
Sunflower seed cake meal . . . . .	0.058	1.5920
Turnip parings . . . . .	0.046	1.6123

As mentioned above, when Schmöger's method is used to estimate molasses the residue obtained from 5 g. of dried ground substance is further used to estimate the fat. Peculiar difficulties are met with in washing feeding stuffs which contain linseed meal as absorbent. In such cases the fat is estimated by the following method, described by Hissink:—<sup>1</sup>

Five grams of the dried and ground feeding stuff, 75 c.c. of concentrated hydrochloric acid, and 75 c.c. of water are gently boiled over an asbestos board for two hours on a reflux condenser; the liquid is then allowed to cool, filtered through a previously moistened filter (deprived of fat), the residue washed till free from acid, and dried for four hours in a water-jacketed drying oven at 80° to 85°. The contents of the filter are crushed, placed in a suitable paper cylinder, which is then

<sup>1</sup> *Landw. Versuchs-Stat.*, 1904, 60, 125.

further dried for two hours at nearly  $100^{\circ}$ , and finally extracted with ether for seven hours in the Soxhlet extractor.

The following method for the estimation of the nitrogen not combined as albumin, in molasses (it is also applicable to all other feeding stuffs), is due to Kellner<sup>1</sup>:—Ten grams of molasses are distributed in about 300 c.c. of water, the solution made slightly acid by very dilute sulphuric acid, treated with 20 c.c. of 10 per cent. tannin solution, shaken, diluted with water to 500 c.c., allowed to stand for about twelve hours, and then filtered through an air-dry filter into a dry flask; 200 c.c. of the filtrate are used for the estimation of nitrogen (by Kjeldahl's method). The nitrogen in tannin must be subtracted from the amount of nitrogen found.

Total sugar is estimated as follows:—Twenty-five grams of molasses feeding stuff are placed in a litre flask and covered with water; the liquid is frequently shaken round and diluted to 1000 c.c. after the lapse of one hour. One hundred c.c. of this solution are treated with 30 c.c. of  $N/10$  hydrochloric acid in a 250 c.c. flask, the liquid heated for half an hour on a boiling water-bath, and then allowed to cool; just sufficient dilute sodium or potassium hydroxide is added to neutralise the acid, the flask filled to the mark, and the invert sugar in 50 c.c. of this solution estimated by Meissl-Allihn's method; the method is described in detail in the Section on "Spirits," Vol. III.

The amount of invert sugar obtained is calculated to cane-sugar. It is customary, however, to make a direct determination before inversion and a second after inversion, the difference between the two tests being calculated as cane-sugar. The invert and cane-sugar are returned as "sweetening matters" (Smetham).

The percentage of molasses in the feeding stuff can be calculated from the amount of sugar found, on the assumption that molasses contains 48 per cent. of sugar.

The dried and ground substance is used for the estimation of total albuminoids, crude fibre, and ash; the methods are described above, (I., pp. 448 *et seq.*).

## VI.—EXAMINATION OF PRECIPITATED PHOSPHATES FOR FEEDING PURPOSES

As a rule, the analysis of precipitated phosphates extends only to the quantitative estimation of the total and citrate-soluble phosphoric acid, and to the qualitative recognition of, or in some cases the accurate estimation of, arsenious acid, chlorine, sulphurous acid, carbon dioxide and fluorine. The methods of estimating the phosphoric acid are described in detail in the section on "Manures," pp. 389 and 400.

<sup>1</sup> *Landw. Versuchs-Stat.*, 1900, 53, 115.



Gutzeit recommends the following method for the detection of arsenic in precipitated phosphate:—One to two grams of substance and about 1 g. of chemically pure zinc (free from sulphur and arsenic) are placed in a test tube and covered with dilute hydrochloric acid, free from arsenic; the tube is closed by a plug of wadding and the mouth covered by a piece of filter paper soaked in cold, saturated silver nitrate solution. The appearance, after a short time, of a light yellow stain on the filter paper shows that arsenic is present in appreciable quantity (*cf.* Vol. I., p. 374).

The following method for the quantitative estimation of arsenic is due to Fresenius:—Ten grams of substance and 100 c.c. of concentrated hydrochloric acid (sp. gr. 1.19) are placed in a 500 c.c.

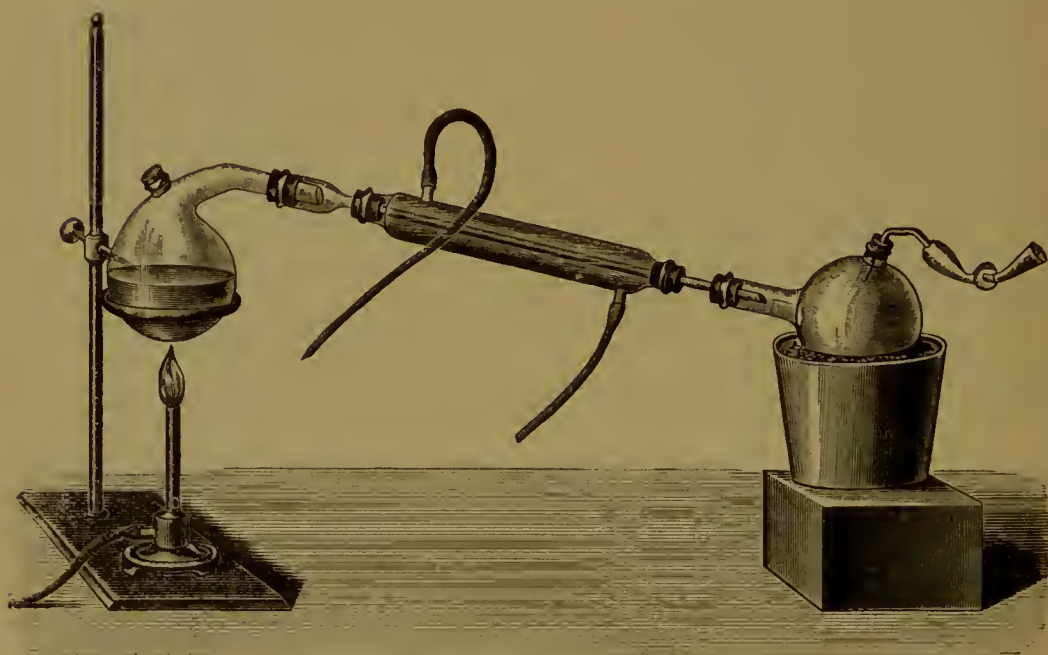


FIG. 72.

retort with a tubulus (Fig. 72), the acid and substance mixed by shaking, 5 c.c. of a cold, saturated ferric chloride solution added, and the contents of the retort distilled till only a small residue remains; 20 c.c. of water are placed in the receiver before distillation. The receiver is connected air-tight to the condenser and to a Peligot tube containing a little water, as shown, and must be well cooled during the distillation. The united contents of the Peligot tube and receiver are then saturated with sulphuretted hydrogen, at first warm, and finally cold, the precipitate filtered after standing for twelve hours, and washed successively with sulphuretted hydrogen, water, alcohol, carbon bisulphide and again with alcohol; it is then dried and weighed as arsenious sulphide ( $\text{As}_2\text{S}_3$ ). As a check, the sulphide is redissolved in ammonia and ammonium carbonate, the solution acidified with hydrochloric acid,

saturated with sulphuretted hydrogen, and the arsenious sulphide again weighed.

Details for the estimation of arsenic are given in Vol. I., pp. 362 *et seq.* As a rule, only small quantities of arsenic are present, and these can be conveniently determined by the Marsh-Berzelius method, as in the estimation of arsenic in brewing materials.

Sulphurous acid is identified by reduction with zinc in hydrochloric acid solution. To estimate it, it is distilled off by heating the phosphate with phosphoric acid solution, collected in a receiver containing iodine solution, and precipitated and weighed as barium sulphate.

Carbon dioxide, chlorine, and fluorine are detected and determined by the usual methods of analysis; fluorine rarely occurs in precipitated phosphate.

## APPENDIX I.

### DIRECTIONS FOR THE EXAMINATION OF FEEDING STUFFS OCCURRING IN INTERNATIONAL TRADE

(Agreed upon by the International Committee for the Analysis of Artificial Manures and Feeding Stuffs at the International Congress of Applied Chemistry, Berlin, 1903.)

#### Preparation of the Samples for Analysis.

As far as possible, a degree of fineness should be aimed at which will enable the whole of the material to pass through a 1 mm. sieve; this applies to all feeding stuffs without exception.

#### Methods of Analysis.

1. **Moisture.**—Five grams of substance are dried at 100° for three hours. In the case of linseed cake, see under 3 (i.).

2. **Albuminoids.**—(i.) *Total Albuminoids.*—Nitrogen is estimated by Kjeldahl's or Gunning-Atterberg's method, and the amount of nitrogen found is multiplied by 6.25. In the case of difficultly decomposable feeding stuffs, *e.g.*, cotton seed meal, groundnut meal, etc., it is advisable to add phosphoric anhydride to the acid if Kjeldahl's method is used.

(ii.) *Pure Albumin* is estimated either by Stutzer's or by Kellner's method. The method used should be stated.

(iii.) *Digestible Nitrogen Compounds.*—These are estimated by G. Kühn's improved modification of Stutzer's method.

Commercial pepsin may be substituted for gastric juice, provided the conditions laid down by Wedemeyer<sup>1</sup> are followed.

**3. Fat.**—(i.) *General Method.*—The feeding stuffs must first be dried for three hours at 95°, on no account above 100°. In the case of linseed cake and other oil cakes containing oils which oxidise easily, the drying must of course be conducted in a current of hydrogen or coal gas, or it must be limited to one hour at 100°. The fat must be extracted with ether free from alcohol and water. The extraction must be complete. The ether extract need not be soluble in ether after drying.

(ii.) *Molasses Feeding Stuffs.*—To estimate the fat, 25 g. of molasses feeding stuff are first dried for about three hours at about 80°, weighed when cold, and then ground; 5 g. of the powder are then placed on a filter or in a Gooch crucible attached to the pump, and extracted with 100 c.c. of cold water, which is allowed to drip slowly on to the substance. The residue is dried at 95° in the usual way and extracted with ether.

**4. Nitrogen Free Extractive Matters.**—(i.) The total of these products is generally taken by difference when all other constituents have been estimated.

(ii.) In the estimation of sugars, the methods agreed upon by the International Sugar Commission are accepted.

**5. Woody Fibre.**—This is estimated by Weender's method of boiling 3 g. of substance (deprived of fat if necessary) with 200 c.c. of 1.25 per cent. sulphuric acid and 200 c.c. of 1.25 per cent. potassium hydroxide. Each boiling must be continued for half an hour from the moment when ebullition commences, and the water evaporated off must be replaced; each boiling with acid or alkali is followed by boiling with water. The residue is thoroughly washed with hot alcohol and then with ether, dried till of constant weight, and weighed. The weight of the ash of the residue is subtracted.

Most of the determinations made by English chemists have been obtained by the use of 125 c.c. of 2 per cent. acid and alkali (Smetham).

**6. Ash.**—Five grams of substance are carefully incinerated at a gentle heat.

**7. Sand or Mineral Admixtures.**—The qualitative examination of all feeding stuffs for sand or mineral admixtures is necessary. These constituents must be quantitatively estimated whenever the preliminary test shows their presence in abnormal quantity. The sender of the sample must be informed of the result if the amount of these admixtures is more than 1 per cent.

<sup>1</sup> *Landw. Versuchs-Stat.*, 1899, 51, 385.



## APPENDIX II.

FERTILISERS AND FEEDING STUFFS (METHODS OF ANALYSIS)  
REGULATIONS, 1908<sup>1</sup>*(Text of the Regulations issued by the Board of Agriculture and Fisheries.)*

The Board of Agriculture and Fisheries, in pursuance of the provisions of the Fertilisers and Feeding Stuffs Act, 1906, hereby make the following Regulations:—

## COMMENCEMENT

1. These Regulations shall take effect on the first day of January 1909, and remain in force until altered or revoked by the Board of Agriculture and Fisheries.

## DEFINITIONS

2. In these Regulations:—

“The Act” means the Fertilisers and Feeding Stuffs Act, 1906.

“Fertiliser” means any article used for fertilising the soil.

“Feeding Stuff” means any article used as food for cattle (as defined by the Act—*i.e.*, bulls, cows, oxen, heifers, calves, sheep, goats, swine, or horses) or poultry.

Other expressions have the same respective meanings as in the Act.

METHODS OF ANALYSIS OF FERTILISERS<sup>2</sup>

3. The Methods of Analysis for the purposes of the Act shall be as follows:—

(1.) PREPARATION OF THE SAMPLE FOR ANALYSIS<sup>3</sup>

(a) In the case of powdered fertilisers in a dry, or moderately dry, condition, the sample shall be passed through a sieve with perforations about 1 mm. in diameter.

Adventitious materials which cannot be conveniently crushed, *e.g.*, fragments of metal in basic slag, shall be removed and allowed for.

(b) Other substances which are dry enough to powder, but which are not in a fine condition, shall be pulverised until the sample passes through a sieve with perforations about 1 mm. in diameter.

<sup>1</sup> *Statutory Rules and Orders*, 1908, No. 964.

<sup>2</sup> The appended notes, in regard to the details of the analysis, have been added by the Reviser.

<sup>3</sup> Details in regard to the taking of samples for the purposes of the Act are specified in “The Fertilisers and Feeding Stuffs (Sampling, etc.) Regulations, 1906” (*Statutory Rules and Orders*, 1906, No. 945).

(c) Wool, hair, hoof, shoddy, and similar substances shall be pulled apart and cut until in a fine condition: or, if dry, they may be passed through a shredding machine.

(d) Moist fertilisers which do not admit of being passed through a sieve shall be thoroughly mixed by the most suitable means.<sup>1</sup>

(e) In the case of horn, shoddy, and other substances which gain or lose water during the process of pulverising, the proportion of water shall be estimated in the coarse and in the powdered condition respectively, and the results of the analysis of the powdered sample shall be calculated to the water content of the original coarse substance.

(f) Crystalline or saline materials, such as sulphate of ammonia, nitrate of soda, or potash salts, may be prepared by being well mixed and rapidly ground in a stoneware mortar, the portion finally reserved for analysis being especially finely ground.

(g) When the sample has been passed through the sieve and thoroughly mixed, or, if not passed through the sieve, has been thoroughly mixed, a part of it, not being less than 100 g., shall be placed in a stoppered bottle, and from this the portions for analysis shall be weighed.

## (II.) DETERMINATION OF MOISTURE (LOSS ON DRYING)

A weighed quantity of the sample shall be dried at 100° C.

## (III.) DETERMINATION OF NITROGEN

The presence or absence of nitrates must first be ascertained.<sup>2</sup>

### (a) *Total Nitrogen in absence of Nitrates.*

A weighed portion of the sample<sup>3</sup> shall be transferred to a Kjeldahl digestion flask; 10 g. of potassium sulphate and 25 c.c. of concentrated sulphuric acid shall be added, and the flask shall be heated until a clear

<sup>1</sup> In the case of large samples, a convenient method is to break up the largest portions and to halve the bulk by "quartering"—*i.e.*, by thoroughly mixing the material and dividing it into four approximately equal portions with a knife or spatula. The two opposite "quarters" are then mixed and the lumps again reduced in size. The process of "quartering" and reduction should be continued until the portion remaining is sufficiently fine for analysis.

<sup>2</sup> This can be conveniently done by adding to the filtered water extract of the manure a few drops of a solution of indigo-carmin in sulphuric acid, and pouring into the mixture about an equal bulk of concentrated sulphuric acid. If the colour is discharged, nitrates are probably present.

<sup>3</sup> The quantity taken must to some extent be determined by the nature and nitrogen-content of the material under examination. With acid and alkali, approximately one-fifth normal quantities, ranging from 1 to 1.2 g., may be taken in the case of materials rich in nitrogen, *e.g.*, dried blood, horn meal, etc., while in the case of many mixed manures and bone meal, quantities up to 3 g. can be conveniently manipulated.

liquid, colourless, or of light straw colour, is obtained.<sup>1</sup> The operation may be accelerated by the addition of a small crystal of copper sulphate, or a globule of mercury to the liquid in the digestion flask.<sup>2</sup>

The quantity of ammonia shall be determined by distillation into standard acid after liberation with alkali, and where mercury has been used, with the addition also of sodium or potassium sulphide solution.<sup>3</sup>

(b) *Total Nitrogen when Nitrates are present.*

A weighed portion of the sample<sup>4</sup> shall be transferred to a Kjeldahl digestion flask: 30 c.c. of concentrated sulphuric acid, containing 1 g. of salicylic acid, shall be added, and the flask shall be shaken so as to mix its contents without delay. The shaking shall be continued at intervals during ten minutes, the flask being kept cool, and then 5 g. of sodium thiosulphate and 10 g. of potassium sulphate shall be added. The flask shall be heated until the contents are colourless or nearly so. Copper sulphate or mercury may be used as above described in paragraph (III.) (a).

(c) *Nitrogen in the form of Ammonium Salts.*

A weighed portion of the sample<sup>5</sup> shall be transferred to a distilla-

<sup>1</sup> It is a safe precaution to heat the potassium sulphate to a red heat before use, and it is better to add it after the frothing with sulphuric acid has ceased. The liquid should be colourless on cooling.

<sup>2</sup> If mercury be used, about 0.7 g. is sufficient. This can be measured in a tube drawn out like a pipette with a mark on the drawn out portion at a point which has been found by experiment to deliver the requisite quantity. By dipping this tube into a bottle of mercury, the proper amount is easily obtained, and can be transferred to the digestion flask.

<sup>3</sup> The use of mercury is preferable to that of sulphate of copper; the decomposition is then often complete in half an hour, and seldom takes longer than one hour. Great care must be exercised, however, not to hurry this stage of the process, and the boiling must proceed briskly. The digestion flask should be placed at an angle, and the neck closed with a glass stopper, loosely fitting, as described on p. 376. By the use of the glass stopper, any undecomposed sulphuric acid is condensed and the risk of the solution boiling to dryness avoided.

The distillation apparatus should be provided with a proper condensing arrangement and should have a "trap" of suitable design to prevent any of the alkali used from being carried over into the standard acid. A simple and efficient contrivance for this purpose consists of a piece of  $\frac{3}{8}$ -inch block tin tubing, carried to a height of a foot or 18 inches above the distillation flask before being connected to the condenser. The steam is partially condensed in the tube and the condensed water carries back to the distillation flask any of the alkali which may have been carried up during ebullition. A little granulated zinc placed in the distillation flask prevents bumping.

The distillation flask should be provided with a stoppered funnel to allow of the addition of the alkali without loss of ammonia, and the sulphide solution should be added *after* the alkali, otherwise there is a risk of sulphuretted hydrogen being evolved.

Direct distillation with a flame is preferable to distillation by means of a current of steam, as in the latter case some of the ammonia may escape distillation.

<sup>4</sup> In many cases it is necessary, and in most cases desirable, to grind the weighed portion of the substance with a small quantity of ignited gypsum before treatment.

<sup>5</sup> In the case of sulphate of ammonia and other ammonium salts, the weighed quantity should not be less than 1 g., and preferably should be greater. A sufficiency of standard acid must, of course, be used.



tion flask, and the quantity of ammonia shall be determined as above prescribed in paragraph (III.) (a).

(d) *Nitrogen in Nitrates in the absence of Ammonium Salts and of Organic Nitrogen.*

One gram of the sample shall be placed in a half-litre Erlenmeyer flask, with 50 c.c. of water. Ten grams of reduced iron and 20 c.c. of sulphuric acid of 1.35 sp. gr. shall be added. The flask shall be closed with a rubber stopper, provided with a thistle tube, the head of which shall be half filled with glass beads. The liquid shall be boiled for five minutes, and the flask shall then be removed from the flame, any liquid that may have accumulated among the beads being rinsed back with water into the flask. The solution shall be boiled for three minutes more, and the beads again washed with a little water. The quantity of ammonia shall then be determined as above prescribed in paragraph (III.) (a).

(e) *Control Experiment in the determination of Nitrogen.*

The materials used in any of the methods described under this paragraph (III.) shall be examined as to their freedom from nitrogen by means of a control experiment, carried out under similar conditions, with the same quantities of the reagents which have been employed in the actual analysis, as in the case of (a), 1 g. of pure sugar being used in place of the weighed portion of the sample. The quantity of standard acid used in the control experiment shall be deducted from the total quantity of acid found to have been neutralised in the distillation of the sample.<sup>1</sup>

(IV.) DETERMINATION OF PHOSPHATES .

(a) *Phosphates Soluble in Water.*

In the case of superphosphates, dissolved bones, and similar substances, 20 g. of the sample shall be continuously agitated for thirty minutes in a litre flask with 800 c.c. of water.<sup>2</sup> The flask shall then be filled to the mark, and again shaken, and the contents shall be filtered. Fifty c.c. of the filtrate shall be boiled with 20 c.c. of concentrated nitric acid, and the phosphoric acid shall be determined by the molybdate method prescribed below in paragraph (IV.) (d).

<sup>1</sup> By the proper selection of reagents, and particularly of the sulphuric acid, the total correction need not exceed 0.1, or at most 0.2 c.c. of one-fifth normal acid. By the simple expedient of testing samples of the sulphuric acid offered by dealers before purchasing, this correction can quite well be kept within these limits.

<sup>2</sup> In the case of moist or sticky fertilisers which will not pass through a sieve of the prescribed mesh, it is necessary to break up the material with water before transferring it to the flask for agitation.

In the case of fertilisers in which the proportion of phosphates soluble in water is small, a larger quantity of the filtrate, prepared as above, shall be taken.

(b) *Phosphates Soluble in the Prescribed Citric Acid Solution.*

Five grams of the sample shall be transferred to a stoppered bottle of about 1 litre capacity. Ten grams of pure, crystallised citric acid shall be dissolved in water, the volume shall be made up to 500 c.c., and the solution shall be added to the weighed portion of the sample in the bottle. To lessen the possibility of caking, the portion of the sample in the bottle may be moistened with 5 c.c. of alcohol or methylated spirit before the citric acid solution is added; and in that case the volume of the citric acid solution shall be 495 c.c. instead of 500 c.c. The bottle shall be at once fitted into a mechanical shaking apparatus, and shall be continuously agitated during thirty minutes. The solution shall then be filtered through a large "folded" filter, the whole of the liquid being poured on the paper at once. If not clear, the filtrate shall be again poured through the same paper.

Fifty c.c. of the filtrate shall be taken and the phosphoric acid shall be determined by the molybdate method prescribed below in paragraph (IV.) (d).

(c) *Total Phosphoric Acid.*

A weighed portion of the sample, in which portion, if necessary, the organic matter has been destroyed by ignition and the silica removed by appropriate means shall be dissolved in nitric acid and boiled, the solution being made up to a definite bulk. The phosphoric acid shall be determined in an aliquot part of the solution by the molybdate method prescribed below in paragraph (IV.) (d).

(d) *Molybdate Method.*

To the solution, which should preferably contain from 0.1 to 0.2 g. of phosphoric oxide ( $P_2O_5$ ), obtained as above described in paragraphs (IV.) (a), (b), or (c), 100 to 150 c.c. of molybdic acid solution, prepared as described below, or an excess of such solution, *i.e.*, more than is sufficient to precipitate all the phosphoric oxide present in the solution, shall be added, and the vessel containing the solution shall be placed in a water-bath, maintained at  $70^\circ$  for fifteen minutes, or until the solution has reached  $70^\circ$ . It shall then be taken out of the bath and allowed to cool, and the solution shall be filtered, the phospho-molybdate precipitate being washed several times by decantation, and finally on the paper with 1 per cent. nitric acid solution. The filtrate and washings shall be mixed with more molybdic acid solution and allowed

to stand for some time in a warm place in order to ascertain that the whole of the phosphoric oxide has been precipitated.

The phospho-molybdate precipitate shall be dissolved in cold, 2 per cent. ammonia solution, prepared as described below, and about 100 c.c. of the ammonia solution shall be used for the solution and washings. Fifteen to twenty c.c. of magnesia mixture prepared as described below, or an excess of such mixture, *i.e.*, more than sufficient to precipitate all the phosphoric oxide present, shall then be added, drop by drop, with constant stirring. After standing at least two hours, with occasional stirring, the precipitate shall be filtered off, washed with 2 per cent. ammonia solution, dried, and finally weighed as magnesium pyrophosphate.<sup>1</sup> The filtrate and washings shall be tested by the addition of more magnesia mixture.

(e) *Preparation of the Molybdic Acid Solution.*

The molybdic acid solution shall be prepared as follows:—One hundred and twenty-five grams of molybdic acid and 100 c.c. of water shall be placed in a litre flask, and the molybdic acid shall be dissolved by the addition while the flask is shaken, of 300 c.c. of 8 per cent. ammonia solution, prepared as described below. Four hundred grams of ammonium nitrate shall be added, the solution shall be made up to the mark with water, and the whole added to 1 litre of nitric acid (sp. gr. 1.19). The solution shall be maintained at about 35° for twenty-four hours and then filtered.

(f) *Preparation of Magnesia Mixture.*

The magnesia mixture shall be prepared as follows:—One hundred and ten grams of crystallised magnesium chloride and 140 g. of ammonium chloride shall be dissolved in 1300 c.c. of water. This solution shall be mixed with 700 c.c. of 8 per cent. ammonia solution, and the whole shall be allowed to stand for not less than three days and shall then be filtered.

(g) *Preparation of the Ammonia Solutions.*

The 8 per cent. ammonia solution shall be prepared as follows:—One volume of ammonia solution of sp. gr. 0.880 shall be mixed with three volumes of water. This solution shall then be adjusted by the addition thereto of more strong ammonia solution, or water as required, until the specific gravity of the solution is 0.967.

The 2 per cent. ammonia solution shall be prepared as follows:—One volume of 8 per cent. ammonia solution shall be mixed with three volumes of water.

<sup>1</sup> The washing in this case must be complete. Washing once or twice by decantation before transferring the precipitate to the filter will be found advantageous.



## (V.) DETERMINATION OF POTASH

(a) *Muriate of Potash free from Sulphates.*

A weighed portion of the sample (about 5 g. in the case of concentrated muriate of potash, or 10 g. in the case of low grade muriate) shall be dissolved in water, the solution shall be filtered if necessary, and made up to 500 c.c. To 50 c.c. of the solution, placed in a porcelain basin, a few drops of hydrochloric acid shall be added, and also 10 c.c. or 20 c.c. (according to whether the portion weighed was 5 g. or 10 g.) of a solution of platinum chloride containing 10 g. of platinum per 100 c.c. After evaporation to a syrupy consistency on a water-bath, the contents of the basin shall be allowed to cool, and shall then be treated with alcohol of sp. gr. 0.864, being washed by decantation until the alcohol is colourless. The washings shall be passed through a weighed or counterpoised filter paper, on which the precipitate shall be finally collected, washed with alcohol as above, dried at 100°, and weighed.

The precipitate is to be regarded as  $K_2PtCl_6$ .

(b) *Salts of Potash containing Sulphates.*

A weighed portion of the sample (about 5 g. in the case of concentrated sulphate of potash, or 10 g. in the case of kainite or other low-grade salts) shall be boiled with 20 c.c. of hydrochloric acid and 300 c.c. of water in a half-litre flask. Barium chloride solution shall be cautiously added, drop by drop, to the boiling solution until the sulphuric acid is completely precipitated. Any slight excess of barium shall be removed by the addition of the least possible excess of dilute sulphuric acid. The liquid (without filtration) shall be cooled and made up to 500 c.c. A portion shall then be filtered, and 50 c.c. of the filtrate shall be treated as in paragraph (v.) (a), 10 c.c. or 20 c.c. of platinum chloride solution, as the case may be, being used.

(c) *Potash in Guanos and Mixed Fertilisers.*

Ten grams of the sample shall be gently ignited in order to char organic matter, if present, and shall then be heated for ten minutes with 10 c.c. of concentrated hydrochloric acid, and finally boiled with 300 c.c. of water. The liquid shall be filtered into a half-litre flask, raised to the boiling point, and a slight excess of powdered barium hydroxide shall be added.<sup>1</sup> The contents of the flask shall be cooled, made up to 500 c.c., and filtered. Of the filtrate, 250 c.c. shall be treated with ammonia solution and excess of ammonium carbonate, and then, while

<sup>1</sup> It is preferable to add the barium hydroxide in the form of a saturated solution; it should be added to very distinct alkaline reaction.

boiling, with a little powdered ammonium oxalate, cooled, made up to 500 c.c. and filtered. Of the filtrate, 100 c.c. are to be evaporated in a platinum dish, and the residue heated, first in the air-bath and then very gently over a low flame, till all ammonium salts are expelled, the temperature being carefully kept below that of low redness.<sup>1</sup> The residue shall be treated with hot water, filtered if necessary, and the potash shall be determined in the filtrate as in paragraph (v.) (a).

#### METHODS OF ANALYSIS OF FEEDING STUFFS

4. The methods of analysis of a feeding stuff for the purposes of the Act shall be as follows :—

##### (I.) PREPARATION OF THE SAMPLE<sup>2</sup>

(a) If the sample is already in a fine condition, *e.g.*, a meal, it shall be thoroughly mixed, and a portion for the determination of moisture shall be at once taken.

(b) If the sample is not in a fine condition, *e.g.*, a cake, it shall be carefully pulverised until the whole passes through a sieve with perforations from 2 to 3 mm. in diameter. It shall then be thoroughly mixed, and a portion for the determination of moisture shall be at once taken.

(c) From the sample thus prepared, a portion of not less than 100 g. in weight shall be taken and further powdered if necessary and passed through a sieve with perforations of about 1 mm. in diameter.

(d) If the original sample is appreciably damp, or if for any reason the operations of pulverisation and mixing are likely to result in loss or gain of moisture, the moisture shall be determined in this portion, as well as in the sample prepared as in paragraph (I.) (b), in order that the results of the analysis may be corrected to correspond with the sample in its original condition as regards moisture.

(e) Materials which cannot be conveniently pulverised or passed through a sieve shall be thoroughly mixed and sampled by the most suitable means.

(f) The prepared portion of the sample shall be placed in a stoppered bottle and from it the portions for analysis shall be weighed.<sup>3</sup>

<sup>1</sup> This operation should be conducted with the greatest care, and the ignition should be carefully watched the whole time, so as to stop the heating directly the ammonium salts are volatilised. A good plan to adopt is to carry the sides of the dish through the flame until the alkalis are just in a state of incipient fusion.

<sup>2</sup> Details in regard to the taking of samples for the purposes of the Act are specified in "The Fertilisers and Feeding Stuffs (Sampling, etc.) Regulations, 1906" (*Statutory Rules and Orders*, 1906, No. 945).

<sup>3</sup> The portions taken for the various tests are best obtained by "quartering" until reduced to approximately the weight required (*cf.* p. 470).

## (II.) DETERMINATION OF MOISTURE (LOSS ON DRYING)

A weighed quantity of the sample shall be dried at 100° C.

## (III.) DETERMINATION OF OIL

(a) A weighed quantity<sup>1</sup> of the sample shall be placed in a Soxhlet thimble, which has been placed in the Soxhlet extraction tube and extracted with washed, redistilled ether. At the end of three to four hours<sup>2</sup> the thimble shall be removed from the Soxhlet tube, dried, and its contents finely ground in a small mortar previously rinsed with ether. The substance shall then be returned to the thimble, the mortar being washed out with ether, and the extraction continued for another hour.<sup>3</sup>

After evaporation of the solvent, the oil shall be dried at 100° and weighed.<sup>4</sup> The oil shall be redissolved in ether, and any undissolved matter shall be weighed and deducted.<sup>5</sup>

(b) In the case of samples containing saccharine matter, *e.g.*, sugar meals, the weighed portion in the Soxhlet thimble shall be washed twice with water and then dried, previous to extraction.<sup>6</sup>

## (IV.) DETERMINATION OF ALBUMINOIDS

The percentage of albuminoids shall be ascertained by multiplying the percentage of nitrogen by 6.25.

The determination of nitrogen shall be as follows:—A weighed portion<sup>7</sup> of the sample shall be transferred to a Kjeldahl digestion flask: 10 g. of potassium sulphate and 25 c.c. of concentrated sulphuric acid shall be added, and the flask heated until a clear liquid, colourless,<sup>8</sup> or of a light straw colour, is obtained. The operation may be accelerated by the addition of a small crystal of copper sulphate or a globule of mercury to the liquid in the digestion flask.

The quantity of ammonia shall be determined by distillation into

<sup>1</sup> About 3 g. is the most convenient quantity.

<sup>2</sup> The distillation should be at such a rate that the ether syphons freely, but not sufficiently quickly to endanger loss of oil by spirting on the cork.

<sup>3</sup> Time is saved by substituting a second flask in the second extraction.

<sup>4</sup> A series of weighings should be made at intervals of half an hour or so until the weight is practically constant.

<sup>5</sup> By putting part of the ether in the flask and preventing syphoning until distillation commences, the danger of carrying over particles of the meal is prevented.

<sup>6</sup> Medicated meals containing sulphur, distillery meals containing lactic acid, condiments containing turmeric and other substances, may yield ether extracts not wholly consisting of fatty matters. Matters other than oils and fatty acids should be determined and specified in the report.

<sup>7</sup> From 1 to 1.5 g. is a convenient quantity.

<sup>8</sup> In the case of feeding stuffs which are free from any appreciable quantity of iron, the resulting solution should be quite colourless.



standard acid after liberation with alkali, and, where mercury has been used, with the addition also of sodium or potassium sulphide solution.

The materials used shall be examined as to their freedom from nitrogen by means of a control experiment carried out under similar conditions with the same quantities of the reagents which have been employed in the actual analysis, 1 g. of pure sugar being used in place of the weighed portion of the sample. The quantity of standard acid used in this control experiment shall be deducted from the total quantity of acid found to have been neutralised in the distillation of the sample.<sup>1</sup>

#### USE OF PRESCRIBED WEIGHTS

5. In calculating the results of analysis the atomic weights adopted by the International Committee on Atomic Weights shall be employed.

#### FORMS OF CERTIFICATES

6. Every certificate which is affected by Regulation No. 3 of the Fertilisers and Feeding Stuffs (General) Regulations, 1906, and these Regulations, and which is dated on or after the first day of January 1909, shall contain the following words:—"The analysis was made in accordance with the Fertilisers and Feeding Stuffs (Methods of Analysis) Regulations, 1908."

#### LIMITS OF ERROR

For the purposes of the provisions of the Act, concerning the effect, as a warranty of the statements made in the invoice, of a fertiliser or of a feeding stuff, respecting the percentages of phosphates, nitrogen, and potash contained in the fertiliser, or of oil or albuminoids contained in the feeding stuff, the limits of error shall be as follows:—<sup>2</sup>

#### FERTILISERS

*Note.*—In this schedule the figures relating to limits of error represent percentages of the whole bulk.

*Example of Application of Schedule.*—*E.g.*, in the case of a bone compound, if the percentages stated in the invoice are: soluble phosphates, 20; insoluble phosphates, 8; nitrogen, 1; then the warranty implied under sec. 1 (1) of the Act will be that the fertiliser contains: soluble phosphates, 19 to 21 per cent.; insoluble phosphates, 7 to 9 per cent.; nitrogen, 0·7 to 1·3 per cent.

<sup>1</sup> See directions for the Estimation of Nitrogen in Fertilisers, p. 471.

<sup>2</sup> "The Fertilisers and Feeding Stuffs (Limits of Error) Regulations, 1906" (*Statutory Rules and Orders*, 1906, No. 946).

Description of Fertiliser.	Limits of Error.			
	Soluble Phosphates.	Insoluble Phosphates.	Nitrogen.	Potash.
1. Superphosphate . . . . .	1	...	...	...
2. Dissolved bones (vitriolised or vitriolated) made from raw bones and acid only :—				
(I.) When the total of the percentages of phosphates (soluble and insoluble) stated in the invoice amounts to 32 or more, then—				
(a) If the excess of the actual percentage of insoluble phosphates over that stated in the invoice is 3 or more . . . . .	4	...	.3	...
(b) If such excess is not less than 2, but is less than 3 . . . . .	3	...	.3	...
(c) If such excess is not less than 1, but is less than 2 . . . . .	2	...	.3	...
(II.) In all other cases . . . . .	1	1	.3	...
3. Bone compounds . . . . .	1	1	.3	...
4. Compound manures (other than bone compounds, but including dissolved or equalised guano) :—				
(a) If the respective percentages of nitrogen and potash stated in the invoice do not exceed 4 . . . . .	1	1	.3	.3
(b) If such respective percentages exceed 4 . . . . .	1	1	.5	.5
5. Sulphate of ammonia . . . . .	...	...	.5	...
6. Nitrate of soda . . . . .	...	...	.5	...
7. Ground hoofs and horns . . . . .	...	...	.5	...
8. Dried blood . . . . .	...	...	.5	...
9. Fish guano and meat meal . . . . .	...	2	.5	...
10. All cakes and meals (other than bone or meat meal). . . . .	...	...	.5	...
11. Ground bones and bone meal . . . . .	...	2	.5	...
12. Basic slag and basic superphosphate . . . . .	2*	2	...	...
13. Shoddy, wool, and hair waste . . . . .	...	...	1	...
14. Kainite and other potash salts :—				
(a) Where the percentage of potash stated in the invoice does not exceed 15 . . . . .	...	...	...	1
(b) Where such percentage exceeds 15 . . . . .	...	...	...	2
15. Nitrate of potash . . . . .	...	...	.5	2
16. Peruvian and other natural imported guanos :—				
(a) Where the percentage of insoluble phosphate stated in the invoice does not exceed 30 . . . . .	...	3	...	.5
(b) Where such percentage of insoluble phosphate exceeds 30 . . . . .	...	5	...	.5
(c) Where the percentage of nitrogen stated in the invoice does not exceed 3 . . . . .	...	...	.5	.5
(d) Where such percentage of nitrogen exceeds 3 and does not exceed 5 . . . . .	...	...	.75	.5
(e) Where such percentage of nitrogen exceeds 5 . . . . .	...	...	1	.5

\* That is, soluble in a solution of citric acid of the prescribed strength.

## FEEDING STUFFS

*Note.*—In this Schedule the percentage of albuminoids is to be taken as the percentage of nitrogen multiplied by 6.25.

*Example of Application of Schedule.*—*E.g.*, in the case of a linseed cake, if the percentages stated in the invoice are: oil, 10; albuminoids, 30; then the warranty implied under sec. 1 (2) of the Act will be that the linseed cake contains: oil, 8.75 to 11.25 per cent.; albuminoids, 26.25 to 33.75 per cent.

Description of Feeding Stuff.	Limits of Error.
Decorticated cotton cake or meal . . . . .	One-tenth of the percentage of oil and one-tenth of the percentage of albuminoids stated in the invoice.
Undecorticated cotton cake or meal . . . . .	
Earth nut or ground nut cake or meal . . . . .	
Palm kernel or palm nut cake or meal . . . . .	
Cocoanut cake or meal . . . . .	
Niger seed cake or meal . . . . .	
Sesame seed cake or meal . . . . .	
Sunflower seed cake or meal . . . . .	
Hemp seed cake or meal . . . . .	
Kurdee or safflower cake or meal . . . . .	One-eighth of the percentage of oil and one-eighth of the percentage of albuminoids stated in the invoice.
Compound cakes and meals . . . . .	
Linseed cake or meal . . . . .	
Rape cake or meal . . . . .	One-fifth of the percentage of oil and one-fifth of the percentage of albuminoids stated in the invoice.
Maize products . . . . .	
All other feeding stuffs (as above defined in Regulation 2) not otherwise specified in this Schedule . . . . .	

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# EXPLOSIVES

By the late OSCAR GUTTMANN. English translation revised by the Author.<sup>1</sup>

## A. RAW MATERIALS

### I.—POTASSIUM NITRATE

#### (a) Crude Nitre.

THE analysis of crude nitre is scarcely ever carried out in explosives factories, since the nitre is now always obtained in the refined state. The analysis is conducted as described in Vol. I., p. 539; the method used for the examination of sodium nitrate, Vol. I., pp. 307 *et seq.*, may also be referred to.

The "official" method formerly used in Germany was based upon a purification of the nitre on a small scale. The amount of potassium in the residual salts was then determined by the perchlorate method (Vol. I., p. 522), and a further sample converted to carbonate by fusion with charcoal and sodium chloride, the carbonate decomposed by hydrochloric acid and the amount of nitrogen originally present as nitrate calculated from the loss of weight. No special precautions were taken to dry the gas. This method could perhaps give a rough approximation as to the yield which might be expected in refining the nitre, but could scarcely be considered as a serviceable analytical method. The same observation applies to the following French method:—

*French Method.*—Two samples, each of 400 g., are taken from the nitre, which has been brought up to 90 to 94 per cent., by breaking up the crystals and washing them with water or mother liquors. The samples are covered with 500 c.c. of water previously saturated with nitre at 12°·5, stirred for ten minutes, allowed to settle, and poured on

<sup>1</sup> This section, which was written by the late Mr Oscar Guttman, both for the first and second German editions, has been considerably added to by Dr E. Berl in the third German edition (vol. iii., 1911). The English translation was revised by Mr Guttman in 1910, when he did not regard it as desirable to incorporate the additions proposed by Dr Berl for the third German edition, in the English translation. The translation has accordingly been left as revised by Mr Guttman.—C. A. K.

to a filter. A second washing is carried out in the same way with 250 c.c. of saturated nitre solution. These operations must be carried out in a room, the temperature of which is constant, to avoid solution or separation of nitre. After drying, the filter is carefully laid upon a double sheet of blotting paper resting upon some absorbent material such as filter paper cuttings, chalk, etc., in a flat dish. After twenty-four hours, the nitre is scraped off, dried on a sand-bath, and weighed. The difference of weight, divided by four, gives the percentage of impurities; 2 per cent. must be added to the value thus obtained to allow for insoluble matter and nitre remaining from the saturated solution. The method is tedious and inaccurate.

### (b) Refined Saltpetre.

The limit for the proportion of sodium chloride in pure saltpetre is 0.005 per cent. in England and 0.010 per cent. in Germany and in France (in France, for blasting powder, 0.033 per cent.). To test this, a few grams are dissolved in water by warming, and silver nitrate added; at most, a faint opalescence should result.

In France, 5.03 g. of silver nitrate, previously fused, are dissolved in 520 c.c. of water (1 c.c. = 0.0033 g. of sodium chloride). One hundred grams of the sample are dissolved in distilled water, diluted to 500 c.c., and three portions of 50 c.c. removed (each portion = 10 g. saltpetre). To these the silver nitrate solution is added, drop by drop, from a pipette (thirty drops = 1 c.c.), six drops being added to the first portion, eight to the second, and ten to the third. The solutions are shaken, and a portion of each is filtered through a well-washed filter which has been tested with silver nitrate. One drop of silver nitrate solution is added to each of the three filtrates, and the degree of purity is judged by the turbidity (six drops =  $\frac{1}{15000}$ , ten drops =  $\frac{1}{9000}$  of impurity). A control test is always made by adding a drop of sodium chloride solution to nine drops of the filtrate, to ascertain whether excess of silver nitrate has been added. For mining powder, one part of impurity in 3000 is permissible.

It is to be assumed from the presence of such a small quantity of sodium chloride, that other impurities are also present only to about the same extent, but Hellich showed, in 1894, that potassium perchlorate may at times be present in considerable quantities. In Germany it is now required that saltpetre shall not contain more than 0.2 per cent. of perchlorate, although according to the experiments of Lenze and Bergman, 0.5 per cent., and of Dupré as much as 1 per cent. may be considered harmless. The official regulations in France require for artillery and rifle powder not more than  $\frac{1}{10000}$  of potassium chlorate; and for artillery powder not more than  $\frac{1}{1000}$ , and for rifle powder not more than  $\frac{3}{1000}$  of perchlorate.

Sulphates and carbonates are tested for qualitatively by barium chloride; calcium, and magnesium salts, by the addition of ammonia and potassium oxalate or sodium phosphate, and sodium nitrate is tested for on the blowpipe or by covering the sample with alcohol and burning. Impurities can also be detected microscopically by allowing the salt-petre to crystallise out from a saturated solution, evaporating the mother liquor, crystallising the residue a few times, and examining the final mother liquor under the microscope. Potassium nitrate crystallises in prisms, sodium nitrate in rhombohedra, potassium and sodium chlorides in cubes which have the form of steps.

For the quantitative analysis, the *Moisture* is determined by heating a weighed quantity in a platinum crucible until it just melts, allowing to cool in an exsiccator, and weighing. A further 100 g. of saltpetre are dissolved in water, in a beaker covered with a watch-glass, the solution filtered through a dried and weighed filter, and the residue washed, dried, and weighed. This gives the so-called "*Insoluble Matter*." The *Chloride* is determined by dissolving 10 g. in hot water and titrating with *N*/10 silver nitrate solution, using potassium chromate as indicator, until a permanent red precipitate results. One c.c. corresponds to 0.005846 g. sodium chloride (*cf.* Vol. I., p. 123). The quality of pure nitrate is further determined, as a check, with Lunge's nitrometer (Vol. I., pp. 132 and 315).

In France, two different methods are prescribed for the determination of *Chlorate*. In the first test a comparison is made of the intensity of the yellow coloration which results when nitrate containing chlorate is added to sulphuric acid of sp. gr. 1.84. Comparative tests are made with 0,  $\frac{1}{1000}$  and  $\frac{1}{10000}$  of chlorate, a known weight of nitrate, free from chlorate, being treated with the required quantities of a solution of potassium chlorate (1 g. per litre) and then dried and powdered. Four to five c.c. of pure sulphuric acid of sp. gr. 1.84 are placed in four similar watch-glasses standing on a sheet of white paper, and the standard nitrates and finally the nitrate to be tested are added, one by one, to the acid in the watch-glasses. This addition is made in such a way that the nitrate forms a cone projecting from the sulphuric acid. The colorations of the solid masses are compared with the standard sample after standing for half a minute.

In the alternative method, 10 g. of nitrate are dissolved in 50 to 60 c.c. of water, four to five drops of neutral silver nitrate solution (10.8 g. per litre) added to precipitate any chlorides present, and the solution filtered repeatedly until perfectly clear. The filtrate is tested for chlorides with a drop of silver nitrate solution, heated to 90°, 15 to 20 c.c. of an aqueous solution of lead nitrite then added, and the turbidity removed by the addition of 5 to 10 c.c. of nitric acid (pure acid of sp. gr. 1.33 diluted with an equal volume of water). If the liquid does not



remain clear the nitrate contains chlorates, and is then tested to ascertain whether the quantity exceeds  $\frac{1}{10000}$ , by applying the same procedure to distilled water to which known quantities of potassium chlorate solution have been added; in both cases similar beakers are used and the same volumes of the solutions (*cf.* Vol. I., p. 322).

For the determination of *Perchlorate* a large number of methods have been proposed, which are described in Vol. I., pp. 319-322. The following very accurate method is due to Dupré.<sup>1</sup> Twenty grams of the sample are melted for an hour at 545° (excluding the time of heating up to this temperature) in covered nickel crucibles of about 70 c.c. capacity in a Gilbert's air-bath. The 20 g. sample is dissolved in warm water and transferred to a 200 c.c. flask with the help of a funnel. The solution is best effected by the gradual addition of small quantities of water, 200 c.c. in all, the heating being carried out uniformly to avoid loss of liquid. Finally, the crucible and cover are washed, the solution allowed to cool, and diluted to 200 c.c. The chlorine is determined in 25 c.c. by Mohr's method (Vol. I., p. 123) as a preliminary test. One hundred c.c. of the solution are taken (or less, if the preliminary test shows that more than 25 c.c. of a silver solution, corresponding to 0.001 g. Cl per cubic centimetre are required), sufficient silver nitrate of this strength added to precipitate all the chloride, then 4 c.c. of pure, concentrated nitric acid, and the solution heated for half an hour on a sand-bath to near the boiling point, actual ebullition being avoided. The solution is cooled, carefully filtered, the precipitate washed, some iron alum added to the filtrate, and the silver titrated with ammonium thiocyanate by Volhard's method (Vol. I., p. 123). The thiocyanate solution is prepared so as to be about half the concentration of the silver solution; near the end of the titration, two drops or a multiple of two are always added, so that the colour change appears very distinctly; the exact amount required is ascertained by deducting half of the last number of drops added.

A second sample of 10 g., which has not been previously heated, is then titrated as a preliminary determination by Mohr's method, the heating of the solution being avoided as far as possible, and a further titration is carried out by Volhard's method with a third sample of 10 g. previously melted for an hour at 545°, as in the case of the original 20 g. sample. The difference in the chlorine before and after heating gives the quantity of perchlorate, if no other chlorine compounds are present. If the nitrate contained more than a trace of magnesia, the weighed sample must be moistened in the crucible with a few drops of sodium hydroxide, and dried in an air-bath, before commencing the fusion; if iodates are present, they must be determined and allowed for in the results. Instead of titrating, the silver chloride on the filter

<sup>1</sup> *J. Soc. Chem. Ind.*, 1902, **21**, 825.

paper may be weighed, but if this be done special attention must be paid to the washing, as otherwise nitrate may remain behind and would considerably influence the results.

In Lenze's<sup>1</sup> method the sample is melted at 580° to 600° instead of at 545°.

According to the French official method for the determination of perchlorates, 10 g. of dry nitrate are weighed into an uncovered platinum crucible, about 10 g. of sodium carbonate, free from chloride, added, the two salts mixed with a platinum wire and gradually heated to melting, the crucible being covered. The fusion must take place quietly and completely, and the cover must not be lifted. After a quarter of an hour the flame is removed and the covered crucible allowed to cool. If the fusion has been carried out successfully the whole forms a solid mass, adhering to the bottom of the crucible without any particles having been thrown up to the sides. To ascertain the size of flame necessary to effect this, a parallel blank experiment is carried out in which the lid of the crucible is lifted from time to time to ascertain the progress of the fusion. It is first ascertained qualitatively whether the percentage of perchlorate is less than 0.1. For this purpose the fused mass is dissolved in pure nitric acid diluted with an equal volume of water, avoiding spirting by covering the crucible with a watch-glass and allowing the acid to flow in from a pipette between the watch-glass and the rim of the crucible until no further effervescence occurs. The liquid in the crucible must react distinctly acid to litmus. It is then transferred to a 250 c.c. flask, both crucible and cover being thoroughly washed out with water. The solution is made up to 250 c.c., the whole shaken, and 50 c.c. removed with a pipette divided in  $\frac{1}{10}$ th c.c. In a few cubic centimetres of pure nitric acid 1.56 g. of pure silver are dissolved and diluted to a litre (1 c.c.=2 mg. perchlorate). Sufficient of this solution is added to the above 50 c.c. to correspond to the maximum content of 0.1 per cent. perchlorate (and, in addition, the maximum of  $\frac{1}{10000}$  of chloride). The liquid is shaken, filtered repeatedly through a filter paper previously washed with nitric acid, until the filtrate is clear, and the filtrate tested with hydrochloric acid and silver nitrate, to ascertain whether the nitrate contained more or less than the permissible maximum. The determination may be repeated with the remainder of the solution, or the perchlorate may be determined quantitatively.

## II.—SODIUM NITRATE (CHILI SALTPETRE)

The qualitative and quantitative methods for the analysis of sodium nitrate are fully described in Vol. I., pp. 306 *et seq.* In English, German,

<sup>1</sup> *International Congress of Applied Chemistry Report*, 1903, 2, 394.

and American works the determination of the nitric-nitrogen is generally carried out by Lunge's method (Vol. I., p. 315); in France, Schlösing's method (Vol. I., p. 317) is used.

Good sodium nitrate for the preparation of nitric acid should contain at least 96 per cent. of pure sodium nitrate, and not more than 0.75 per cent. of sodium chloride. The quantity of nitrate available for the preparation of nitric acid,  $x$ , is found from the quantity of nitric oxide,  $a$ , obtained in the nitrometer, by deducting one molecule of sodium nitrate for every molecule,  $b$ , of sodium chloride, in accordance with the equation:—

$$x = a - \frac{b \times 85.01}{58.46} = a - (b \times 1.454).$$

When sodium nitrate is used as an addition to explosives, it is repeatedly crystallised, and should then contain not more than  $\frac{1}{10000}$  of chlorine. The test is carried out in the same way as for potassium nitrate.

### III.—AMMONIUM NITRATE

This has almost always an acid reaction. It is tested qualitatively by heating a small quantity, when ammonia is evolved. The nitrogen content is determined in Lunge's nitrometer, and the acidity by titration with sodium hydroxide, using methyl orange as indicator. A red colour indicates the presence of iron, which is determined in the usual way.

### IV.—BARIUM NITRATE

This is tested for qualitatively by the green flame coloration to which it gives rise in the Bunsen burner. It is examined quantitatively in the same way as potassium nitrate.

### V.—POTASSIUM CHLORATE, SODIUM CHLORATE, POTASSIUM PERCHLORATE, AND AMMONIUM PERCHLORATE

These substances are only used by a few works. Minute quantities of impurities only are admitted because, if present, they may enter into combination with other constituents of the explosives; the conditions of purity are usually fixed by each works.

### VI.—SULPHUR<sup>1</sup>

A finely ground sample is boiled with distilled water and tested for acid by dipping a piece of litmus paper into the solution. Sulphur which reacts acid must be again ground and washed. When burnt in a porcelain crucible under a bell-jar, it should leave no residue (earths

<sup>1</sup> Cf. Vol. I., pp. 264 *et seq.*



and oxides). In Great Britain refined sulphur must not give more than 0.15 per cent. of residue, and in America not more than 0.25 per cent.; in France and Switzerland no residue is permitted, and in France crude sulphur of third quality must not give more than 3 per cent. of residue.

A bright yellow or reddish colour indicates arsenic, the presence of which is not permitted. It is tested for by prolonged boiling with nitric acid, decanting the liquid, neutralising the residue with ammonium carbonate, and adding silver nitrate, when no yellow precipitate should be formed. The sulphur may also be treated with aqueous ammonia, and hydrochloric acid then added; no yellow precipitate of arsenic sulphide should result.

#### VII.—CHARCOAL

The examination is, in general, confined to the physical properties. Good charcoal has a deep black, velvety fracture, does not scratch polished copper, and should ring well when struck. Brown charcoal is recognised by its colour, whilst charcoal which has been too strongly ignited is hard, and has a metallic ring. Dogwood charcoal has a dense fracture and a round brown pith; willow charcoal a black round pith; alder a triangular pith, and hazelwood a small, round black pith. If a quantitative examination is required, the charcoal is oxidised in the usual way to carbon dioxide and water in a tube, and the contained carbon and hydrogen calculated. The nitrogen and oxygen are found by difference after deducting the ash.

#### VIII.—WOOD MEAL

Wood meal is used as an addition to dynamite, and less frequently as an ingredient of powders. It should be free from acid, and is generally required in such a state of subdivision that it passes through a sieve of twenty meshes per linear centimetre. It is tested for combustibility by mixing one part of wood meal with three parts of potassium nitrate in a wooden mortar and igniting in a covered crucible. The residue should not exceed 10 per cent. The rapidity of combustion is tested by filling a portion of this mixture into a metal groove and igniting at one end.

One of the best European explosive factories specifies the following requirements for wood meal. It must be prepared from white wood free from resin. In its preparation no chemicals or other cleansing or bleaching agents must be used. The wood meal must be free from impurities, and special care must be taken that no nails or other metal particles are present. The moisture must not exceed 5 per cent. The meal must pass through a sieve of twenty meshes per linear centimetre,

but not more than a third of it must pass through a sieve of forty meshes. In drying, it must not be exposed to any acid vapours, or to too high a temperature, in order to avoid the presence of acetic or other acid or of any undesirable, volatile ingredient.

### IX.—NITRIC ACID<sup>1</sup>

The requirements of nitric acid used for the manufacture of nitroglycerine, guncotton, etc., are that it shall contain at least 94 per cent. of monohydrate, and not more than 1 per cent. of nitric peroxide, and that it shall be free from chlorine and sulphates. In many works, however, nitric acid is used containing from 92 to 96 per cent. monohydrate and not more than 0.75 per cent. nitric peroxide. The English Government calculates the nitrous acid as  $\text{HNO}_2$ , not more than 1.5 per cent. being allowed. This method of calculation is not quite accurate, for concentrated nitric acid contains no nitrous acid, but nitric peroxide. Since, however, the latter yields equal molecules of nitric and nitrosyl-sulphuric acid when mixed with concentrated sulphuric acid, and the nitric acid which thereby results is available for nitration purposes, the method is quite rational, as it only gives the nitrous acid, which is useless for the nitration.

The acid is tested qualitatively for chlorine, sulphates, and iron in the usual way. Nitrous acid is always present if the acid is not quite white.

Quantitative tests are carried out for:—

(a) *Nitric Acid Monohydrate*, by weighing out some water into a 100 c.c. flask with a ground stopper, then adding 10 c.c. of the nitric acid from a pipette, weighing again, and diluting to 100 c.c. The mixture is carefully shaken, 10 c.c. withdrawn, and titrated with  $N/10$  sodium carbonate solution, using methyl orange as indicator. More exact results are obtained by weighing out about 2 g. into a flask as above, diluting, and titrating the whole (*cf.* Vol. I., p. 329).

(b) *Nitrous Acid* (nitric peroxide).—The method given by Lungc is now universally applied. Somewhat less than the required quantity of  $N/10$  permanganate is introduced into a small Erlenmeyer flask, and exactly 2 c.c. of the nitric acid allowed to flow in, drop by drop, from a pipette, with continual shaking, the pipette being held immediately over the permanganate solution. The solution is diluted with water, and titrated further with permanganate until the red colour persists for at least a minute (*cf.* Vol. I., p. 328). One c.c.  $N/10$  permanganate corresponds to 0.00460 g. nitric peroxide. The weight of nitric peroxide found is divided by the specific gravity of the sample of nitric acid and multiplied by 100, and gives then the weight per volume of nitric peroxide in percentages of monohydrate.

<sup>1</sup> *Cf.* Vol. I., pp. 323 *et seq.*

## X. SULPHURIC ACID

This must contain at least 96 per cent. of monohydrate, but it is often stipulated that it shall contain 97 per cent. It must be free from iron and other mineral matter, and must not contain arsenic. It is examined quantitatively by titrating a weighed quantity with  $N/10$  sodium carbonate solution, using methyl orange as indicator. On passing hydrogen sulphide through a mixture of 50 g. of the acid and 800 c.c. of distilled water, no yellow precipitate of arsenic sulphide should result.

## XI.—NITRATING AND SPENT ACIDS

(Cf. Vol. I., pp. 331 *et seq.*)

## XII.—CELLULOSE

(a) **Cotton.**—This must be free from husks, seeds, and other foreign matter, and from short fibres and dust. In England, crude cotton must not give more than 1.1 per cent. of fat on extraction for four hours in a Soxhlet apparatus with 100 c.c. of ether, and must not evolve more than 8 per cent. of moisture when dried at  $100^{\circ}$  in an air oven; some German works make more stringent stipulations. Well-purified cotton should not react alkaline, and should sink to the bottom within two minutes when brought into distilled water. It should contain only traces of chlorine, lime, magnesia, iron, sulphuric acid, and phosphoric acid. Immediately before nitration the cotton should not contain more than 0.5 per cent. of moisture. The content of ash should not exceed 0.8 per cent.

To estimate the content of *Wood Gum*, 300 c.c. of sodium hydroxide solution of exactly 5 per cent. strength are poured on to 15 g. of dried cotton, the whole allowed to stand for twenty-four hours, with frequent shaking, and then filtered; to 100 c.c. of the filtrate, 200 c.c. of 95 per cent. alcohol are added, then 9.5 c.c. of hydrochloric acid of sp. gr. 1.19 and the mixture neutralised by  $N/1$  hydrochloric acid, using phenolphthalein as indicator. An excess of 5 c.c. of normal hydrochloric acid is then added, and after allowing the whole to stand for twenty-four hours, the precipitate collected on a dried and weighed filter paper, washed successively with 95 per cent. alcohol and ether, dried at  $100^{\circ}$ , and weighed. The content of wood gum should not exceed 2.5 per cent.

(b) **Wood Cellulose** should possess good absorbent properties and not be pasty. Calculated on the dry substance, the content of ash should not exceed 1 per cent., that of fat not 0.5 per cent., and that of gum not 1 per cent.



In many cases it is desirable to estimate the degree of bleaching; this can be ascertained approximately by the Schwalbe-Vignon copper method.<sup>1</sup>

The proportion of oxy-cellulose can be determined colorimetrically by digesting 0.5 g. of cellulose with 200 c.c. of methylene blue solution (0.005 g. in 100 c.c.) for twenty-four hours, and estimating the amount of colouring matter left in the solution by means of a Krüss or other colorimeter.

### XIII.—GLYCERINE

This must have a specific gravity of at least 1.262, and must be free from calcium, sulphuric acid, chlorides, arsenic, sugar, and other impurities. It should be transparent and only very faintly coloured, and must contain no free acid except traces of fatty acids. When rubbed on the hand, it should give no unpleasant smell; at most, it should only smell of caramel. When mixed in equal parts with a 10 per cent. solution of silver nitrate it should give no black precipitate after ten minutes. It is sometimes required that, when mixed with a quarter of its volume of 10 per cent. silver nitrate solution and allowed to stand for fifteen minutes in the dark, no dark brown coloration should be formed, and that when mixed with its own volume of normal Fehling's solution it should show no reduction after standing for twelve hours in the dark. When nitrated with one part of nitre and two parts of sulphuric acid, the resultant nitroglycerine must separate readily after ten minutes and be free from flocculent particles. If the nitroglycerine is poured into water, the latter must not become turbid and must become clear at once after the washing. The specific gravity is determined with a Sprengel pyknometer. Qualitative tests are further made for chlorine with silver nitrate, for sulphuric acid with barium chloride, for calcium with ammonium oxalate, and for fatty acids by the above silver test. The organic and inorganic residues are estimated by gradually evaporating 25 g. of the glycerine in a platinum dish on a water-bath or sand-bath below 160°, until the residue is fairly thick, and then completing the evaporation in an air-bath at 160°. According to Schalkwijk, a little water should be added to the residue from time to time to prevent it from becoming too thick. After evaporating to dryness, the residue is allowed to cool in an exsiccator, and weighed. This gives the sum of the organic and inorganic impurities. The residue is then incinerated by igniting the platinum dish, and again weighed, after cooling in an exsiccator. The residual ash gives the quantity of inorganic matter, and the difference between this and the previous weighing the quantity of organic impurity. The former should not exceed 0.25 per cent. and the latter 0.10 per cent. It is

<sup>1</sup> *Z. angew. Chem.*, 1910, 23, 924; *J. Soc. Chem. Ind.*, 1910, 29, 689.

sometimes required that a 50 per cent. solution shall give no precipitate when treated with nitric peroxide and heated for two hours on a water-bath; also that no precipitation should occur on further dilution.

To nitrate the glycerine, the mixed acids are placed in a beaker, which is held with the hand in a pail of cold water and kept continuously in motion, and the glycerine slowly allowed to flow in. When the nitration is complete, the mixture is brought into a separating funnel and the nitroglycerine which separates run out into a long burette. The residual acid is run into a second burette and both are allowed to stand for half an hour. The number of cubic centimetres of nitroglycerine, multiplied by the sp. gr. 1.600, gives the weight of nitroglycerine obtained. This should be at least 200 per cent. of the glycerine.

Special apparatus for conducting the nitration test are also used in German works, of which that devised by Schlegel and improved by Novak<sup>1</sup> is the most convenient. This consists of a separating funnel which is placed in a suitable containing vessel; the funnel is provided with an inlet tube for air, an exit tube, and a thermometer. A freezing mixture or well-cooled water can be used with this apparatus, whereby any decomposition is avoided as far as possible.

#### XIV.—BENZENE, TOLUENE, NAPHTHALENE, PHENOL

(*Cf.* section on Coal Tar, pp. 779 *et seq.*)

#### XV.—KIESELGUHR

The commercial product is usually sufficiently pure. The quantity of organic matter is found by ignition. Oxides of iron, aluminium sulphate, and other impurities are tested for in the usual way. The absorbing power is tested by mixing a weighed quantity of nitroglycerine with a weighed quantity of kieselguhr, filling the mixture into a wooden mould, and pressing with a wooden plunger loaded with a given weight. The mould is open at both ends, and its lower opening closed with a piece of parchment paper. No nitroglycerine should exude when a certain pressure is applied, generally 10 kg. per square cubic metre for a column 10 cm. high.

#### XVI.—MINERAL JELLY

This is principally used in England for the manufacture of cordite. It should be free from foreign matter, scales, and particles, should have a flash-point of at least 400° F. (205° C.) and a specific gravity of not less than 0.87 when tested with a hydrometer at 100° F. (37.8° C.). When

<sup>1</sup> *Z. ges. Schiess- u. Sprengstoffw.*, 1906, 1, 23, 191. The apparatus is made by E. Greiner, Stützerbach.

exposed in an open dish over boiling water, it should not lose more than 0.2 per cent. in twelve hours. The melting point should not be lower than 86° F. (30° C.), and it should be free from both mineral matter and acids.

#### XVII.—CAMPHOR

Natural camphor is completely soluble in alcohol and in ether. In the pure state it melts at 179°·4; the commercial, usually sublimed product melts at about 177°. It should leave no residue on combustion, and should contain only a minute quantity of insoluble matter. The examination of camphor has been investigated by J. E. Crane and C. M. Joyce.<sup>1</sup>

#### XVIII.—ACETONE

The commercial product is now very pure. It is distinguished by its characteristic smell, which is, however, common to methylethylketone and other acetone oils. According to Schwicker,  $\frac{1}{10000}$  per cent. of acetone can be detected by adding a few drops of ammonia of specific gravity 0.890 and two drops of *N*/10 iodine solution to the solution, when a cloudy precipitate of nitrogen iodide is formed, which on shaking or gentle warming disappears, giving rise to a precipitate of iodoform.

In England it is required that the liquid shall be genuine acetone containing only small quantities of substances which are normally formed as by-products. It must be colourless and perfectly transparent, give no turbidity when mixed with water in any proportion, and no residue when evaporated on the water-bath. The specific gravity at 15°·5 must not exceed 0.800. When 1 c.c. of a 0.10 per cent. solution of pure potassium permanganate is added to 100 c.c. of acetone at 15°·5 a distinct colour must remain for at least thirty minutes. Further, it must not contain more than 0.002 per cent. of carbon dioxide, and must be quite neutral.

In Germany and Austria it is specified that:—

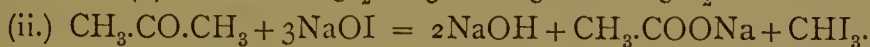
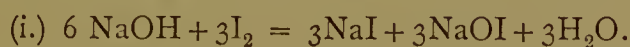
1. The acetone must be completely clear and water-bright.
2. It must be perfectly miscible with water in all proportions, and the mixture shall show no turbidity or precipitate, either at once or on long standing.
3. It shall be perfectly neutral.
4. It shall show at least 98.5 per cent. with the weight-thermoalcoholometer at 15°.
5. It shall not contain more than 0.1 per cent. of aldehyde.
6. The iodometric determination of the iodine shall show at least 98 per cent. of pure acetone.
7. At least 95 per cent. of the acetone shall distil over at 58°.

<sup>1</sup> *J. Soc. Chem. Ind.*, 1907, 26, 386, 598.

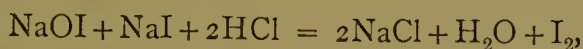


The testing of the acetone by the weight-thermo-alcoholometer is carried out in the apparatus constructed by G. H. Schulze. For the determination of the aldehyde, 3 g. of crystallised silver nitrate, 3 g. of sodium hydroxide, and 20 g. of ammonia solution (sp. gr. about 0.900) are made up to 100 c.c. with water; this solution can be kept for a considerable time in the dark. Ten c.c. of the acetone are treated with 10 c.c. of distilled water and 2 c.c. of the above silver solution, covered, allowed to remain in the dark for half an hour, the liquid then decanted from the reduced silver, and tested with a solution of ammonium sulphide, which should be as light in colour as possible, to ascertain whether any excess of silver remains in solution. If this be the case, the quantity of aldehyde in the acetone is less than 0.1 per cent. The excess of silver is also shown by a brownish black precipitate or a brown turbidity of the solution.

The iodimetric determination of acetone was first described by Krämer. In presence of alkali and excess of iodine, acetone is converted quantitatively to iodoform at the ordinary temperature, according to the following equations:—



Hence 6 atoms of iodine convert 1 mol. of acetone to 1 mol. of iodoform. Thus 58.04 g. of acetone correspond to 761.52 g. of combined iodine. The iodine which does not enter into reaction remains in the form of sodium iodide and hypoiodite as in (i.), and can be again liberated by hydrochloric acid,



and can be estimated by sodium thiosulphate.

For the analysis, about 4 g. of acetone are accurately weighed out and diluted to 1 litre with water. Ten c.c. of this solution are introduced into a 250 c.c. flask with a well-ground stopper, in which they are treated with 50 c.c. of normal sodium hydroxide solution, and 50 c.c. of *N*/10 iodine solution. The mixture is well shaken for half an hour, 50 c.c. of normal hydrochloric acid added, and the free iodine titrated with *N*/10 sodium thiosulphate solution, using a clear starch solution as indicator, until the colour disappears. The thiosulphate used is recalculated to iodine and deducted from the 50 c.c. used. The difference is expressed in percentage by weight of acetone; 1 g. of acetone corresponds to 1033.8 c.c. of *N*/10 iodine solution.

The acidity is tested by adding a few drops of phenolphthalein solution to 100 c.c. of the acetone, and introducing 1 c.c. of *N*/10 sodium hydroxide solution, when a distinct red colour should result. A solution of mercuric chloride should give no turbidity in acetone.

The English specifications for the testing of acetone for acidity

prescribe that 50 c.c. of acetone shall be diluted with 50 c.c. of distilled water and 2 c.c. of phenolphthalein solution added (1 g. in 1000 c.c. of 50 per cent. alcohol). The solution is then titrated with *N*/100 sodium hydroxide solution; 1 c.c. corresponds to 0.0006 g. of acetic acid.

According to A. Marshall,<sup>1</sup> basic substances and strong acids can be determined by diluting the acetone with an equal volume of boiled, distilled water, adding two to four drops of a saturated aqueous solution of para-nitrophenol, and titrating with normal acid or alkali hydroxide respectively. Weak acids can be estimated by mixing the sample with water as above, boiling for from five to ten minutes, and titrating with normal sodium hydroxide, using phenolphthalein as indicator. Carbon dioxide is determined by diluting the acetone with water and titrating with phenolphthalein as indicator, but without boiling.

The accurate determination of the boiling point of acetone requires some care. From 80 to 100 g. of the sample are weighed into a small dry flask of about 150 c.c. capacity, which is placed on a sheet of asbestos 20 cm. square and 5 mm. thick, in the middle of which a hole 20 to 25 mm. in diameter has been cut out. The flask is heated over a free flame. As the bottom of the flask is about 40 mm. in diameter, it completely covers the hole and is protected on all sides from radiant heat by the asbestos. The distillate is collected in a tared flask and weighed. From the quantity taken and that collected, the percentage which passes over at the correct boiling point is calculated.

#### XIX.—ETHYL ETHER AND ETHYL ACETATE

In both cases the commercial products are sufficiently pure. It is sufficient to test them for free acid by the method given under acetone and to ascertain by evaporation whether any residue or foreign odour remains. (For more detailed tests, *cf.* Vol. III.)

#### XX.—ALCOHOL

This may be obtained commercially in a state of sufficient purity. (For the methods of testing, *cf.* Vol. III.)

#### XXI.—DIPHENYLAMINE

This is estimated as diphenylamine tetrabromide, according to the method proposed by W. Dreger.<sup>2</sup> Bromine is added, drop by drop, to an alcoholic solution of diphenylamine, until an excess is present, then twice the volume of water, and the whole boiled, with constant stirring, until the alcohol and excess of bromine have been

<sup>1</sup> *J. Soc. Chem. Ind.*, 1904, 23, 646.

<sup>2</sup> *Z. ges. Schiess- u. Sprengstoffw.*, 1909, 4, 123; *J. Soc. Chem. Ind.*, 1909, 28, 489.

driven off and the liquid reduced to half of its original volume. The precipitate of tetrabromdiphenylamine is filtered off on a Gooch crucible, washed with warm water, and dried at 98° to 100°, until the weight is constant. The percentage of diphenylamine is given by the formula :—

$$x = \frac{34.87 \times n}{s}$$

in which  $n$  = weight of tetrabromdiphenylamine found.  
 $s$  = weight of substance taken.

## B. FINISHED EXPLOSIVES

### I.—BLACK POWDER

#### (a) Qualitative Examination.

The physical properties of the powder are first examined. It should show no differences of colour even when pulverised between the fingers, and no sharp particles should be detectable. When poured over the hand or over a sheet of paper, no colour should be produced. The grains must be hard, and, on grinding, the powder should first break into sharp-edged fragments. The size of the grains should lie between certain limits according to the nature of the powder. These are tested by passing it through a series of sieves.

The "volumetric gravity," that is the weight of a litre of powder, is determined by a standard litre measure. The absolute specific gravity is generally determined by Bianchi's densimeter, and that of large-grained or prismatic powder by Bode's densimeter.

The moisture content is determined by drying the sample in an air-bath or on a water-bath. The temperature is retained at 160° F. (71° C.) in England, 85° to 90° C. in Germany, and 70° C. in France. The powder is tested qualitatively by extracting a small quantity on a filter with hot water, and examining the extract by the method given under saltpetre. Sulphur is extracted by pouring carbon bisulphide over a small sample, decanting, and evaporating the liquid in a small porcelain dish, when crystals of sulphur are obtained. The charcoal is separated by digesting a small quantity of the powder with carbon bisulphide, filtering, washing the residue with hot water, drying the filter, and examining the residue under a microscope.

#### (b) Quantitative Examination.

1. *Saltpetre*.—Five grams of the powder are brought on to a filter, moistened with water, and the saltpetre dissolved out completely by the addition of small quantities of hot water. After carefully



evaporating the solution, it is finally taken to dryness at  $280^{\circ}$  and the residue weighed.

2. *Sulphur*.—In Great Britain and France, Millon's method is used. One part of the powder is oxidised by slowly heating it with eleven parts of pure, concentrated nitric acid and two parts of pure potassium chlorate. When the evolution of gas ceases, a fresh, small quantity of potassium chlorate is added, and this repeated until the liquid is quite clear and yellowish, the nitric acid which is lost by evaporation being replaced. Finally, the whole of the nitric acid is evaporated off, the residue dissolved in hot water, barium chloride added, and the precipitate treated as usual.

The method in general use in Germany is that of Gay-Lussac:—Five grams of finely ground powder are mixed with the same quantity of gently ignited sodium carbonate, 5 g. of potassium nitrate and 30 g. of sodium chlorate added, the whole intimately mixed in a mortar, and then subjected to prolonged heating in a platinum crucible until it is white. After cooling, the mass is dissolved in water, acidified with hydrochloric acid, and the resultant sulphuric acid precipitated with barium chloride (*cf.* Vol. I., p. 272). The precipitated barium sulphate is collected on a filter, carefully washed, dried and weighed, and the sulphur content calculated.

Petersen<sup>1</sup> has proposed the following method for the determination of the sulphur:—0.8 g. of powder is boiled for twenty minutes with 40 c.c. of a 2 per cent. solution of sodium hydroxide, 50 c.c. of a 3 per cent. solution of chemically pure hydrogen peroxide then added, the whole boiled for five minutes, acidified with hydrochloric acid, and filtered. The sulphate formed is evaporated to remove nitric acid, and then precipitated, as usual, as barium sulphate. If the solution be not thus evaporated, about 0.1 per cent. too much sulphur is found.

3. *Charcoal*.—The percentage of charcoal is usually found by difference of weight. In Germany it is prescribed that the residue on the filter from the determination of the nitrate, containing charcoal and sulphur, shall be replaced in the funnel, and the latter placed in a metal funnel kept at  $30^{\circ}$  to  $40^{\circ}$  by warm water. Pure carbon bisulphide, to which 25 per cent. of alcohol has been added, is then poured on to the filter. The washing is finished with pure alcohol, and the filter dried at  $90^{\circ}$  and weighed. The weight obtained, minus that of the filter paper, gives the quantity of charcoal, and the difference that of sulphur.

## II.—NITROCELLULOSE

### (a) Qualitative Examination.

It is generally possible to ascertain with a lens, or if necessary with a microscope, whether the product under investigation contains nitro-

<sup>1</sup> *Z. anal. Chem.*, 1903, 42, 406.

cellulose. According to Kindt, guncotton can be distinguished from cotton by treating with a solution of iodine in potassium iodide and subsequently moistening with dilute sulphuric acid; cotton becomes blue, guncotton yellow. If nitrocellulose be examined under a microscope in polarised light, the unnitrated cellulose appears bright yellow to reddish, whereas highly nitrated cellulose is either bright or dark blue. Lower nitrates of cellulose sometimes appear grey.<sup>1</sup> It is important that there shall be no other nitro-compound in the mixture, for it is probable that most of these will be coloured in polarised light. Dinitrotoluene has been shown to behave in the same way as nitrocellulose.

### (b) Quantitative Examination.

For the testing of nitrocellulose, and particularly of guncotton, a systematic method of analysis is always prescribed in the conditions under which the explosive is accepted.

1. *Moisture*.—A carefully prepared sample is taken, rubbed to a powder by hand, and pressed through a fine metal sieve. Small paper trays are made by folding the edges of a piece of paper, and the guncotton is spread out on these, and dried to constant weight at 40° to 50°. All analytical results are calculated on the dried substance.

2. *Ash*.—Five grams of dried nitrocellulose are burnt off in a weighed platinum or porcelain crucible with the addition of some pure paraffin wax. The combustion may be assisted with a glowing platinum wire, in order that the incineration may take place at the lowest possible temperature. The ash is taken up with a solution of ammonium carbonate, and heated repeatedly to 200° until the weight is constant.

3. *Calcium Carbonate*.—In England, 3 g. of dried nitrocellulose are shaken for fifteen minutes with 20 c.c. of  $N/2$  hydrochloric acid diluted with about twice its volume of water. The mixture is filtered, and the nitrocellulose on the filter washed until neutral. Twenty c.c. of  $N/2$  sodium carbonate solution are then added to the filtrate, and the quantity of sodium carbonate neutralised by the  $N/2$  acid estimated.

On the Continent, 5 g. of nitrocellulose are treated with 100 c.c. of water and 25 c.c. of  $N/5$  hydrochloric acid, at 15°. The mixture is boiled for six to seven minutes, filtered, washed repeatedly, the filtrate allowed to cool and titrated with  $N/5$  sodium carbonate solution, using methyl orange or litmus tincture as indicator. From the difference between the number of cubic centimetres of hydrochloric acid and

<sup>1</sup> The contrary statement in Guttman's *Manufacture of Explosives*, vol. ii., p. 59, is due to an erroneous transposition of the words "colourless" and "iridescent." The behaviour in polarised light mentioned by Guttman was taken from Désortiaux, *Les poudres, etc.* Numerous tests of nitrocellulose in polarised light have since been carried out by Guttman, and the question has been systematically studied by Lunge and Weintraub (*Z. angew. Chem.*, 1899, 12, 471).

sodium carbonate used, the alkali content is calculated. Another method is to digest 5 g. of nitrocellulose for twenty-four hours with  $N/2$  hydrochloric acid, filter, wash the residue repeatedly, and dry. The difference of weight gives the quantity of calcium carbonate.

4. *Stability Test*.—About 1 g. is subjected to the stability test described in detail on pp. 512 *et seq.* In England, when used for cordite, it must withstand the test at  $170^{\circ}\text{F.}$  ( $76^{\circ}\cdot7\text{C.}$ ) for ten minutes; in Germany, guncotton must withstand the test at  $80^{\circ}$  for twenty-five minutes. Guncotton containing calcium carbonate is previously freed from this by washing with cold water, or sometimes with dilute hydrochloric acid and then with water, until neutral.

5. *Ignition Temperature*.—0.05 g. of nitrocellulose is brought into a test tube, standing in an oil-bath at  $100^{\circ}$ . The temperature is gradually raised and the point is observed at which the nitrocellulose ignites. For good nitrocellulose this should not be below  $180^{\circ}$ .

A variety of other so-called "Deflagration tests" have also been introduced. A test of this character is employed in Germany in connection with the transport of explosives on railways.

6. *Determination of Nitrogen*.—This is almost always determined with Lunge's nitrometer (Vol. I., pp. 132 and 315). About 0.6 g. of nitrocellulose is accurately weighed into a small weighing bottle, some sulphuric acid added, and the whole allowed to stand for twenty or thirty minutes until the nitrocellulose is completely dissolved. It is then washed into the nitrometer with concentrated sulphuric acid, the bottle rinsed out with a further 10 c.c. of dilute sulphuric acid, and the cup of the nitrometer also washed with this acid. After shaking the nitrometer in the usual way and allowing to cool, the number of cubic centimetres of nitric oxide is read off; the final reading of the temperature should be made after standing for twenty minutes. The statement that by dissolving the guncotton in sulphuric acid cooled with ice, about 0.2 per cent. too much nitrogen is found, has been shown by careful experiments not to be the case.

The French Government uses the Schlösing method, as modified by Schultze and Tiemann and improved by R. Schmidt (*cf.* Vol. I., p. 317). It is not so simple and rapid as Lunge's method, but is used as a control. The apparatus used is shown in Fig. 73.

It consists of a glass cylinder in which a graduated burette is fitted by means of two stoppers. The burette has a glass tap  $a$  and a funnel  $y$  at its upper end; its lower end dips into a glass bath  $w$  which is fitted with a perforated rubber stopper at its lowest point. This is connected by a glass T-piece on the one hand with the vessel containing sodium hydroxide solution and on the other hand with the pressure tube  $c$ . To fill the burette, the glass tap  $a$  and the pinch-cock  $b$  are opened and the sodium hydroxide solution allowed to flow gradually into the



burette, the connection to *c* being kept closed. As soon as the burette is filled and the cup *y* is about half filled, *a* and *b* are closed and *c* opened. Cold water passes through the tube *d* into the lower end of the glass cylinder and passes out through *e*.

To carry out an estimation, from 0.600 to 0.650 g. of nitrocellulose are weighed out into a closed weighing bottle and transferred to the small flask *f*; the weighing bottle is then rinsed out with 25 c.c. of

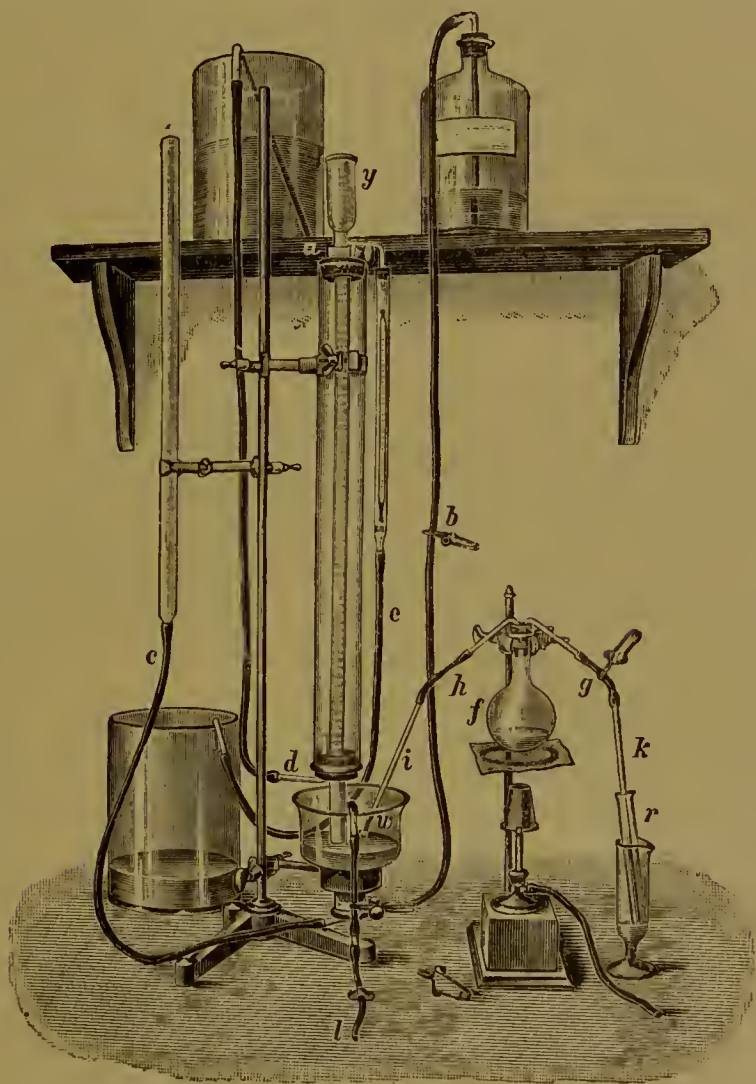


FIG. 73.

water. The flask *f* is fitted with two tubes, one of which passes into the test tube *r* with suitable connections, and the other dips into the bath *w* containing sodium hydroxide solution. By opening and closing the pinch-cocks at *g* and *h* (the pinch-cock at *h* is not shown) the contents of the flask are boiled until free from air. As soon as the air is all driven out, the pinch-cocks *g* and *h* are closed and the flame removed. Twenty-five c.c. of a concentrated solution of ferrous chloride, and 10 to 15 c.c. of concentrated hydrochloric acid, are then introduced

into the tube *r*, and allowed to pass into the flask *f* by opening the pinch-cock *g*, care being taken that no air enters, a few cubic centimetres of water being added to wash in the remains of the hydrochloric acid. The cock *g* is then closed, the tube *i* brought under the burette and the flask heated. As soon as the pressure of the nitric oxide in the flask exceeds the external air-pressure, the rubber connecting tube becomes inflated; the pinch-cock at *h* is then opened, and the contents of the flask boiled, with repeated shaking, until no more bubbles of nitric oxide are evolved and a crackling sound results from the distillation of hydrochloric acid. The pinch-cock *h* is now closed, *g* opened, the burette brought down on to the rubber stopper in the bath *w* so as to make an air-tight connection, and the cooling allowed to proceed until the water which passes out of the cylinder at *e* has the same temperature as that which enters it at *d*, as observed on the thermometers in the glass tube and in the tube *e*. If now the level of the liquid in the pressure tube be adjusted to that in the burette, the volume of nitric oxide can be read to within 0.1 c.c. and the nitrogen content calculated in the ordinary way. The sodium hydroxide solution in the bath is drawn off after use by a tube *l* into a vessel under the table.

The ferrous chloride solution is prepared by dissolving iron nails in hydrochloric acid. The iron must be present in excess. When the evolution of hydrogen ceases, the solution is filtered whilst hot through a folded filter, and the filtrate acidified with a few drops of concentrated hydrochloric acid. The sodium hydroxide solution over which the gas is collected should have a sp. gr. of 1.21 to 1.26.

The results obtained with the Schultze-Tiemann apparatus are generally somewhat higher (about 0.2 per cent.) than those obtained with Lunge's nitrometer. The modification of Kjeldahl's method proposed by Chenel<sup>1</sup> has not come into use.

The nitrogen content is generally expressed as percentage of nitrogen; in France, it is given in cubic centimetres of NO (reduced to 0° and 760 mm.) per gram of nitrocellulose. One c.c. of NO corresponds to 0.0626 per cent. of nitrogen; or, 1 per cent. of nitrogen corresponds to 15.98 c.c. NO. The highest nitrate of cellulose of the formula,  $C_{24}H_{28}(NO_2)_{12}O_{20}$ , should give 14.15 per cent. of N or 226.12 c.c. of NO per gram; a nitrocellulose of this composition has, however, never been obtained (Lunge).

7. *Determination of the Unnitrated Cellulose.*—Five grams of dry nitrocellulose are boiled for half an hour with a saturated solution of sodium sulphide, allowed to stand for twenty-four hours, the solution decanted, then boiled again for half an hour with a fresh solution of sodium sulphide, the residue collected on a linen filter of known weight, washed with hot, distilled water, until the filtrate gives no coloration

<sup>1</sup> *Mémoires des Poudres et Salpêtres*, vol. viii., p. 45.

with lead acetate, then with dilute hydrochloric acid, and finally with water, until the filtrate gives no reaction with silver nitrate. The filter is dried, and the residue detached, and dried on a watch-glass at 50°. The weight of the dried filter minus the weight of the ash, which is determined by igniting the filter in a platinum crucible, gives the weight of the unnitrated cellulose.

In the United States, the nitrocellulose is boiled for thirty minutes with a solution of sodium stannate, allowed to stand for twenty-four hours, the liquid decanted, the residue boiled a second time, filtered on a weighed filter, and washed. It is then washed three or four times with 5 per cent. hydrochloric acid to remove metallic salts, finally with water until neutral, dried, and weighed.

Lunge and Weintraub have proposed the following method for the determination of the unnitrated cellulose:<sup>1</sup>—From 2 to 3 g. of sodium are dissolved in 100 c.c. of alcohol (the proportions are given for about 5 g. of nitrocellulose, for which 2 to 3 g. of sodium form a considerable excess), and if the liquid is not completely clear (owing to impurities in the sodium) it is filtered; 100 c.c. of acetone are then added to this solution. Of the 200 c.c. thus obtained, 50 c.c. are set apart for subsequent use (cf. *infra*), the remaining 150 c.c. are transferred to a porcelain dish or Erlenmeyer flask, and the weighed quantity of nitrocellulose added. The action is assisted by warming on the water-bath to 40° to 50°, with occasional stirring or shaking; after twenty to thirty minutes the reaction is complete. The residue is allowed to subside and the brownish red liquid decanted through a small filter; the residue is moistened with alcohol to remove traces of products resulting from the action of the sodium ethylate upon the acetone, the alcohol decanted, and the residue treated with water, which dissolves the brown substance. The liquid is filtered, the residue brought on to the filter, and well washed with hot water containing some hydrochloric acid. If the quantity of unattacked cellulose is considerable, and if extreme accuracy is not essential, this first estimation is sufficient. The residual cellulose should evolve no gas in the nitrometer, if the reaction has been properly carried out, but should still show a strong diphenylamine reaction, indicating the presence of traces of nitrocellulose, as the brownish red product which is formed in large quantities imbeds the fibres, so that in the first treatment a few fibres escape the action of the mixture. If, therefore, only traces of unattacked cellulose are present in the nitrocellulose under examination, or if it is desired to obtain very accurate results, the residue is subjected to a second treatment. The residue is subsequently washed a few times with alcohol to displace the water, then washed from the filter into a porcelain dish with the 50 c.c. of acetone-ethylate mixture which were set aside initially, again warmed for about

<sup>1</sup> *Z. angew. Chem.*, 1899, **12**, 473.



fifteen minutes to 40° to 50°, filtered through a filter which has previously been dried at 100° and weighed, washed, first with pure water, then with water containing some hydrochloric acid, and finally again with pure water, and dried at 100° and weighed.

The cellulose obtained is almost colourless in the moist state, with a scarcely perceptible tinge of yellow; any more intense coloration is a sign that the analysis has not been correctly carried out. If 0.1 mg. of bleaching powder in water containing hydrochloric acid be brought on to the filter paper, the coloration is destroyed and a snow-white cellulose obtained. A 1 to 3 per cent. solution of hydrochloric acid is used for this treatment, 2 mg. of bleaching powder per 100 c.c. added, and the cellulose moistened with 5 c.c. of this mixture; the cellulose is then washed with water until the filtrate is no longer acid. If the nitro-cellulose contains only small quantities of cellulose (1 to 2 per cent.) the warming with the acetone-ethylate mixture may be dispensed with; for the first treatment ten to fifteen minutes' standing suffices, but in such cases, the subsequent treatment is, as pointed out, necessary. Also, in cases where much cellulose is present, three to four hours' standing at the ordinary temperature may be substituted for the warming; the warming is, however, essential in the subsequent treatment.

8. *Soluble Nitrocellulose*.—The English specification is as follows:—Exactly 50 grains (3.24 g.) of guncotton are brought into a glass cylinder of 200 c.c. capacity, covered with 150 c.c. of ether-alcohol and allowed to digest for six hours with frequent shaking, after which the mixture is allowed to settle. As soon as the liquid above the guncotton is clear, 75 c.c. of the solution are brought into a small, weighed flask, the greater part of the solvent removed by distillation on the water-bath, and the residue dried to constant weight in a water-oven at a temperature not exceeding 120° F. (50° C.).

The weight of the extracted, soluble guncotton, multiplied by 4 gives the percentage of soluble guncotton in the sample.

The method of extracting with ether-alcohol, hitherto used in Germany, Italy, America, etc., gives very inaccurate results.

In the United States,<sup>1</sup> 3 g. of guncotton are allowed to digest for thirty minutes with 50 c.c. of absolute alcohol in a graduated cylinder of 150 c.c. capacity, 100 c.c. of pure ether added, and the cylinder frequently shaken for twelve hours. After allowing to settle, 50 c.c. of the solution are evaporated to dryness in a platinum crucible, and the residue taken as soluble guncotton. As a check method, a second quantity of 50 c.c. is taken, the nitrocellulose precipitated with chloroform and filtered through a weighed filter. The precipitate is redissolved in a mixture of one part of alcohol and two parts of ether, again precipitated with chloroform, dried, and weighed.

<sup>1</sup> W. J. Williams, *J. Frankl. Inst.*, 1899, 147 [3], 209; *J. Soc. Chem. Ind.*, 1899, 18, 526.

An addition of *Mercuric chloride* to guncotton preparations was practised formerly in order to prevent the formation of mould. Since this addition masks the stability test (No. 4, p. 518), its use has led to the rejection of explosives containing mercuric chloride.

A variety of methods have been proposed for the detection of the contained mercury; as the quantities added are extremely small (1 part of mercuric chloride per 10,000 suffices to prolong the stability-test by twenty minutes), very sensitive methods are of necessity required for its detection. In Great Britain the method adopted is to heat the sample and examine the spark spectrum of the evolved vapours. In Germany, the sample is heated in a test tube and the vapours allowed to act on a piece of gold foil, when the presence of mercury is shown by the formation of spots of the amalgam with the gold. This test, which is due to W. R. Hodgkinson, can be made approximately quantitative.

### III.—NITROGLYCERINE AND DYNAMITE

#### Nitroglycerine.

Nitroglycerine seldom comes into commerce as such; at most, it is sometimes met with in alcoholic or acetone solution. The examination of nitroglycerine itself is, therefore, only necessary in works' laboratories. If it is mixed with a solvent, it should be washed with water and filtered through well-dried salt. The moisture is determined by drying in an exsiccator over calcium chloride (*not* sulphuric acid).

Nitroglycerine must be tested for acids and alkalis. For this purpose a sample is treated with distilled water in a separating funnel, well shaken and separated; the addition of a few drops of methyl orange or Congo red shows whether the nitroglycerine is neutral; one to two drops of  $N/4$  hydrochloric acid should at once give the colour change. The nitrogen content is determined with Lunge's nitrometer; if the nitroglycerine is pure and dry, the theoretical percentage (18.51) is found. The nitroglycerine is further tested for stability. In England, nitroglycerine for the manufacture of cordite must withstand the heat test for eighteen minutes at 180° F. (82°.2 C.).

#### Dynamite containing Nitroglycerine simply Absorbed and not Gelatinised.

##### (a) Qualitative Examination.<sup>1</sup>

The sample is treated with dry ether and the residual oil tested by collecting a drop on a piece of filter paper and striking it on an anvil. If the oil be dissolved in alcohol and treated with a solution of ammonium

<sup>1</sup> Cf. Hess, *Mitt. des k. k. Militärkomitees*, 1881,

sulphide in alcohol, a polysulphide is first formed and finally sulphur separates out. If a drop of the oil be added to a solution of ferrous sulphate containing hydrochloric acid and warmed, the nitric oxide reaction is obtained. If a drop of the nitroglycerine be added to a solution of potassium iodide and starch acidified with dilute sulphuric acid and containing a small quantity of zinc filings, the liquid becomes blue. If the oily residue is evidently homogeneous, has a sp. gr. of 1.6 and has no definite smell, it may be considered as containing only nitroglycerine. If impure ether was used the impurities will be found in the residue. If more than traces of sulphur, paraffin, or resin are present they separate out from the nitroglycerine. To test for these impurities, some of the substance which has separated out is collected and pressed between filter paper. The sulphur separates out in the form of crystals, and can be recognised in this way, as also by the smell, and the flame which it gives on ignition. If the extract, after freeing from ether, be treated with cold alcohol, paraffin remains behind. Any resin which is present can be saponified by boiling with sodium carbonate solution, and again isolated from the soap by precipitation with hydrochloric acid. If all three substances are simultaneously present in dynamite, the nitroglycerine is first decanted, and the residue carefully pressed between filter paper. The resin is then separated by boiling with sodium carbonate solution, the residue washed and dried, and part of it treated with aqua regia to convert any sulphur present to sulphuric acid, in which form it is detected by precipitation as barium sulphate; a second portion is boiled with ammonium sulphide, which dissolves out the sulphur, forming ammonium polysulphide. On cooling, the paraffin floats as a crust on the liquid; it is washed, dried, and further tested. The residue from the extraction with ether is afterwards examined, first microscopically for the detection of kieselguhr, wood meal, and charcoal, by the structure and colour. Brown coal and ordinary coal are distinguished by the nature of the products of their dry distillation (brown coal gives acetic acid or ammonium acetate); if the residue is incinerated, any other mineral matter present is found, together with the ash from the coal, and is subjected to analysis by the usual methods.

### (b) Quantitative Examination.

Two methods are in use. Either a weighed quantity of dynamite is introduced into a dried and weighed linen filter in a funnel, and extracted by repeated treatment with ether, or a weighed quantity is digested with ether in an Erlenmeyer flask, with frequent shaking, the whole filtered on a linen filter, washed several times with ether, and the ether extract evaporated at 40° in a weighed beaker on a water-bath; from the moment when the extract becomes turbid it must be watched, and as soon as the turbidity disappears, the beaker is placed under a bell-jar



over calcium chloride, and the jar evacuated to free it from the last traces of ether and moisture.

If paraffin, resin, sulphur, or other such substances are present in the dynamite, as well as nitroglycerine, the extract which has been freed from ether, as above, is weighed, after drying, and heated with sodium carbonate solution on the water-bath. The resin passes into solution and may be separated from the other substances by decanting and washing with distilled water; the resin is then precipitated in this solution by hydrochloric acid, collected on a filter paper previously dried at  $100^{\circ}$ , and washed, dried, and weighed.

In the residue from this operation, the nitroglycerine is dissolved in strong alcohol, the solution decanted, and the residual mixture of paraffin and sulphur washed with strong alcohol, dried, and weighed. In order to separate the sulphur from the paraffin, the mixture is warmed with an aqueous solution of ammonium sulphide, allowed to cool, the paraffin layer pierced, the liquid decanted, and the residual paraffin washed with water, dried, and weighed. The quantity of nitroglycerine and of sulphur is found by the differences.

The residue from the extraction, so far as it consists of substances which are unaffected by heating, is dried in a current of dry air at  $60^{\circ}$  and weighed, then incinerated, and weighed again after cooling, in order to ascertain from the difference whether any traces of organic compounds were present in the residue. If, however, it contains other substances, the residue is first dried on a filter and weighed, then treated with hot, distilled water, the solution evaporated, dried at  $120^{\circ}$ , and the residue weighed. If carbonates are present but no chlorates, the extract is redissolved in water, neutralised with nitric acid, evaporated on a water-bath, dried at  $120^{\circ}$ , and weighed. The carbonates are thus converted to nitrates, without affecting any organic substances present in the extract, and from the difference of the last two weights, the quantity of carbonic acid present is calculated. The dry mass is then ignited, moistened with nitric acid after cooling, freed from the acid, again ignited, and finally weighed, after cooling. All the salts soluble in water are then present as nitrates, but the organic matter is destroyed. The difference between the two last weights gives the quantity of organic matter extracted.

If chlorates are also present in the aqueous extract, the carbonic acid must be determined by precipitation with calcium nitrate, as calcium carbonate, and the chlorate must be determined in a portion of the solution by evaporating, igniting, and precipitating with silver nitrate. The quantity of nitrate is determined in a second portion of the extract by conversion into ammonia. The residue from the extraction with water can only contain charcoal or similar organic substances, and insoluble absorbent materials. The organic matter is removed by

ignition, and the residue weighed, after cooling; the weight of the insoluble mineral matter is thus obtained. If several absorbent substances are believed to be present simultaneously, they may be determined by the usual methods of analysis in the residue. If several organic absorbent substances are present, their quantities can only be estimated approximately by elementary organic analysis.

Dynamite is further tested for stability by the heat test, and also by alternately freezing and thawing three times successively, and by exposing the sample for eight days and nights at a temperature of  $30^{\circ}$  and observing whether any exudation of nitroglycerine occurs. The tendency to absorb water and possibly to separate out nitroglycerine is tested by exposing the dynamite over a vessel containing water under a bell-jar for twenty-four hours.

### **Blasting Gelatine and Gelatine Dynamite.**

Hess gave the following procedure, which is still in general use:—

#### **(a) Qualitative Examination.**

A section is cut from the middle of the cartridge, as finely as possible, in the form of small cubes, with a knife of horn or wood, and treated with a mixture of two parts of anhydrous ether and one part of anhydrous alcohol in a small flask. In this way nitroglycerine, collodion cotton, and any admixtures of camphor, resin, paraffin, and sulphur pass into solution. The extract is treated with excess of chloroform which precipitates the collodion, the supernatant liquid decanted, and the residue pressed between filter paper. The precipitated collodion cotton is recognised by its inflammability, by its explosibility when struck with a hammer on an anvil, and by its behaviour towards sodium sulphide solution, in which it dissolves on boiling. On boiling with ferrous chloride it should give the nitric oxide reaction. The decanted liquid is heated to  $30^{\circ}$ , whereby the bulk of the ether, alcohol, and chloroform is evaporated off, the temperature then raised to  $80^{\circ}$  in order to remove these liquids completely, and the residue treated as described under dynamite. If the presence of trinitrocellulose be suspected in the residue after the removal of chlorates and nitrates, it may be recognised:—

1. By observation under the microscope in polarised light. Trinitrocellulose gives a blue colour whilst unnitrated cellulose has a reddish yellow colour.

2. By boiling the residue with hydrochloric acid and ferrous sulphate, which evolve nitric oxide from trinitrocellulose.

3. By boiling the residue with alcoholic potassium hydroxide and filtering. If the filtrate be rendered faintly acid, free nitric or nitrous acid can be detected.

**(b) Quantitative Examination.**

A sample is prepared, cut into small cubes with a horn spatula, and allowed to stand for five to six days in an exsiccator over calcium chloride for the determination of the moisture.

The best means of separating the nitroglycerine and the collodion cotton from the gelatinous explosive is by treatment with ether-alcohol. Hess proposed Soxhlet's extraction apparatus for this purpose. It has been found, however, that in order to dissolve the nitric esters completely even from a few grams of explosives, the extract must be syphoned off at least fifty times, which requires about twenty-four hours. Notwithstanding all precautions a loss of nitroglycerine by evaporation can scarcely be avoided. This method has recently fallen into disuse, and the explosive (5 g.) is simply placed in a small Erlenmeyer flask, 200 c.c. of ether-alcohol added, and the whole allowed to stand for a few hours with frequent shaking, or allowed to remain overnight. The solution is treated with excess of chloroform, the residual mixture filtered through a dried and weighed linen filter, and the ether-alcohol evaporated off from the filtrate on a water-bath at about 30°; if camphor is present, the residue is shaken with carbon bisulphide. The ether-alcohol extract may also be filtered directly and the nitrocellulose precipitated in the filtrate by chloroform, but this method is inaccurate on account of the gelatinous nature of the solution.

The residue on the filter may still contain nitrocellulose, and also admixtures. It is dried at 60° in a current of air and weighed, and then treated, as described under dynamite, for the determination of soluble salts (saltpetre, chlorates, etc.) and organic extract. A part of the residue is then boiled with a concentrated solution of sodium sulphide, which dissolves the trinitrocellulose, the solution filtered through a weighed filter, and the residue carefully washed with water, dried, and weighed. The quantity of trinitrocellulose is calculated from the loss of weight. Any calcium or magnesium carbonate present is extracted from a further portion of the residue with dilute hydrochloric acid, and the bases determined in the extract, whilst the washed, dried, and weighed residue contains organic and mineral absorbent materials; the latter are determined by incineration. Since the extraction of nitric ester compounds from gelatine dynamite never gives quite accurate results, and the determination of "dope" (absorbing powder) is more conveniently carried out with larger quantities of the sample, it is advantageous to prepare a large quantity of the powder and to take aliquot parts for the determination of the several ingredients. In this way greater accuracy is attained and the analysis requires much less time.



Scheiding proposes treating the blasting gelatine first with ether alone, whereby the nitroglycerine is removed. The nitrate is then extracted with boiling water, and the nitrocellulose separated from the residue with cold ethyl acetate. If the quantity of trinitrocellulose is to be determined, he recommends extracting first with ether-alcohol and then with ethyl acetate.

### Explosives containing Aromatic Hydrocarbons.

These are generally examined by the method given for gelatinised dynamite. The nitrated hydrocarbon is first extracted by a suitable solvent and the admixtures then determined in the usual way.

### Destruction of Samples.

The destruction of samples of dynamite, guncotton, etc., is best effected, as suggested by Dupré, by placing them in the open in long rooms, pouring on petroleum and burning, care being taken that the wind blows the flames away from the samples.

## IV.—PICRIC ACID AND PICRATES

The examination of picric acid includes first the estimation of the pure picric acid, which is best determined from the nitrogen content, which should be 18.35 per cent. This cannot be carried out in the nitrometer; the Schulze-Tiemann method or that of Kjeldahl is used. W. J. Williams<sup>1</sup> has adapted Kjeldahl's method for the analysis as follows:—

One-half gram of the finely powdered sample is brought into a long-necked Kjeldahl digestion flask, 30 c.c. of concentrated sulphuric acid containing 2 g. of salicylic acid, free from nitrogen, poured on, and the whole allowed to stand until the powder has completely dissolved, which frequently requires many hours. When complete solution has been effected, 5 g. of crystallised sodium thiosulphate are gradually added, and the whole slowly warmed until the violent reaction and frothing have ceased. A drop of metallic mercury is then added, and the solution boiled vigorously until the colour is pale amber yellow. In the case of smokeless powders containing picric acid, four to five hours are frequently necessary. Finally, a little potassium permanganate is added to complete the oxidation; this can be greatly accelerated by adding 5 to 10 g. of powdered potassium sulphate, about fifteen minutes after the commencement of the boiling. When the oxidation is complete, the flask is allowed to cool, its contents transferred to a distillation flask, together with 200 c.c. of water and some zinc or platinum to prevent bumping, potassium sulphide solution added to decompose mercury compounds, and then sufficient potassium hydroxide

<sup>1</sup> *J. Franklin Inst.*, 1899, 147, 206.

to render the liquid alkaline. The solution is then boiled and the distillate collected in  $N/2$  acid and titrated with  $N/10$  ammonia.

The melting point is also determined by one of the usual methods; pure picric acid melts at  $122^{\circ}.5$ . The moisture is determined in the usual way, the mineral matter by ignition in an open dish, and the sulphuric acid by careful washing with water and titration. Further, 10 g. of picric acid are boiled with 150 c.c. of water for ten minutes, and the insoluble matter filtered off, dried at  $70^{\circ}$ , and weighed. Finally, the stability is determined by the heat test.

The requirements for good picric acid are that it shall not contain more than 0.3 per cent. of moisture, 0.3 per cent. of mineral matter, 0.2 per cent. of free and combined sulphuric acid, and 0.2 per cent. of insoluble matter. For the heat test, the limit in England is thirty minutes at  $160^{\circ}$  F. ( $71^{\circ}.1$  C.). In analysing ungelatinised preparations containing picric acid, the picric acid is extracted with ether, and the residue examined in the usual way.

In Italy picric acid is tested as follows:—

*Moisture*.—Ten grams of picric acid are heated to  $80^{\circ}$  to  $85^{\circ}$  for two hours. The alteration in weight must not exceed 0.25 per cent.

*Solidifying point*.—A test tube is heated in a glycerine bath and a quantity of picric acid melted in it sufficient to cover the bulb of a thermometer by 2 cm. The picric acid is then allowed to cool, being stirred at the same time with the thermometer. The temperature is read at the moment when the picric acid solidifies; the solidifying point must not be below  $120^{\circ}$ .

*Agglomeration*.—Five grams of picric acid are heated for an hour in a Victor Meyer bath over boiling water and must not show any signs of caking together.

*Residue insoluble in Water*.—Four grams of picric acid are boiled for two minutes with 100 c.c. of water, the insoluble residue collected on a weighed filter and dried to constant weight. The residue must not exceed 0.1 per cent.

*Residue insoluble in Ether*.—The same procedure is followed as above, but with 20 g. of picric acid; the residue must not exceed 0.2 per cent.

*Ash*.—The filter with the ether residue is ignited and weighed.

*Sulphuric acid*.—The aqueous solution from the determination of the residue is diluted to 300 c.c. and divided into three parts. One-third is poured into barium chloride solution; if no turbidity results after fifteen minutes, the experiment is repeated with 10 g. of picric acid. The sulphuric acid content must not exceed 0.05 per cent.

*Chlorine*.—Another third of the above solution is treated with silver nitrate and must not give a precipitate.

*Oxalic acid*.—The third portion is treated with ammonia, acetic acid, and calcium chloride, and must likewise give no precipitate.

## V.—SMOKELESS POWDER

No generally accepted method can as yet be given for the testing of smokeless powders, as special methods are specified by the various Governments in almost every country, and further, the composition of the products varies greatly.

*Preparation of the Sample.*—In all methods of analysis it is of importance to grind the powder as a preliminary operation. This is best done in a mill similar to a coffee mill, with a steel grinding cone. The mill must be put together in such a way that all the parts can be

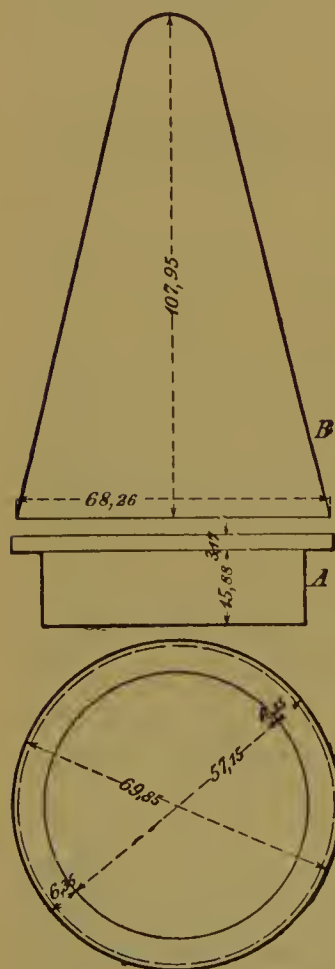


FIG. 74.

readily removed by loosening a few screws, for the purpose of cleaning. In order to guard against contamination of the powder from the mill, a small quantity of the powder is first passed through and discarded. The sample subsequently collected is passed through a sieve and only the portion collected between two sieves is used for the analysis. As an extra precaution, the powder may be brought into the field of a strong magnet, in case any particles of iron may have found their way into it from the mill. The powder is then placed in an exsiccator until its weight is constant, and a further aliquot part is dried at  $60^{\circ}$  to  $70^{\circ}$  to remove all the solvent. In the case of powders containing nitroglycerine the drying should not be prolonged beyond an hour at  $60^{\circ}$ , as nitroglycerine is otherwise lost by evaporation.

*Moisture.*—L. W. Dupré was the first to devise a method for the determination of the moisture in powders containing nitroglycerine. This was improved by A. Marshall and subsequently introduced in the Royal Gunpowder Factory at Waltham Abbey. The term "moisture" indicates all ingredients which are removed from the powder by warming; the

nitroglycerine is, however, completely condensed, and thus only the water and solvent are removed. The apparatus used for this purpose (Fig. 74) consists of an aluminium dish, A, of the dimensions given, and a conical glass cover, B, which must not weigh more than 30 g. The powder is prepared for the determination in the manner described later for the heat test (p. 518). Five grams of the powder retained between the two sieves are weighed



out into the dish, the dish covered with the cone B, the whole accurately weighed, and then brought on to an iron plate, which rests on a water-bath and is heated by the steam. The heating is more prolonged, the more nitrocellulose the powder contains; *e.g.*, for cordite containing 37 per cent., one hour; for cordite containing 65 per cent., two hours are necessary, assuming that the moisture does not exceed 1.3 per cent. After heating, the apparatus is allowed to cool in an exsiccator for half an hour and weighed. The glass cone must not fit tightly, and for this reason the rim of the aluminium dish is somewhat bent in order to allow the water and acetone vapour to escape; the nitroglycerine is deposited completely on the glass cone.

For all further estimations, the powder must be brought into solution. This is best effected with acetone, and if the solution be then strongly diluted with water, the presence of nitrocellulose, nitroglycerine, and other ingredients may be qualitatively detected as described under gelatine dynamite.

### Quantitative Analysis.

It is generally advantageous to effect the solution of the sample step by step. For instance, if the powder contains nitroglycerine, nitrobenzene, nitrotoluene, or other similar compounds, the nitroglycerine, etc., is extracted with ether by treating a weighed quantity in a Soxhlet extractor, or better, in a small Erlenmeyer flask with frequent shaking, until complete solution has taken place, filtering and washing repeatedly with ether. The soluble nitrocellulose is determined in the residue by extracting with ether-alcohol, and the insoluble portion is used for the determination of the insoluble nitrocellulose and unnitrated cellulose. The analysis can, of course, be accelerated, and under some circumstances better results can be attained by using aliquot parts for the determination of the different ingredients. Pure nitrocellulose powder is examined in the same way as guncotton. The nitrogen content is determined in the nitrometer, and it is advantageous to make use of the syphon tube described by Lunge (Vol. I., p. 136, Fig. 44), as smokeless powder only dissolves slowly in sulphuric acid.<sup>1</sup>

### VI.—MERCURY FULMINATE

Mercury fulminate is seldom used alone, being usually mixed with nitre, sulphur, potassium chlorate, or meal powder. If the composition is loaded into caps, it is carefully loosened from the copper case by gentle pressure with a pair of flat pincers. As a precaution, the right hand, by which alone the operation is carried out, should be well wrapped in a cloth, the pincers and cap being covered

<sup>1</sup> Cf. also E. Berl and A. W. Jurissen, *Z. angew. Chem.*, 1910, 23, 241; *J. Soc. Chem. Ind.*, 1910, 29, 374.

with several thicknesses of the end of the cloth, and the opening of the cap should be held downwards so that the loosened fulminating mixture drops out at once. The mercury fulminate is examined by dissolving in ammonia at  $30^{\circ}$  to  $35^{\circ}$ , and the ingredients of the residue then detected and determined separately by the method given under black powder (pp. 495 *et seq.*).

H. Brownsdon<sup>1</sup> has described a volumetric method for the determination of mercury fulminate, based on the observation that this compound is decomposed by sodium thiosulphate with liberation of alkali, which is titrated with *N*/10 sulphuric acid, using methyl orange as indicator. The solution is standardised by pure mercury fulminate, which is obtained from the commercial product by dissolving in potassium cyanide, precipitating with dilute nitric acid, filtering, washing, and drying at  $80^{\circ}$  to  $90^{\circ}$ . Of this 0.04 to 0.05 g. is dissolved in 30 c.c. of water, about 1 g. of thiosulphate added, shaken until dissolved, diluted to 100 c.c. and titrated with the acid in portions of 25 c.c. until the methyl orange changes colour. In this way the quantity of acid is ascertained which corresponds to a given weight of fulminate, and the same acid is then used for the determination of mercury fulminate in caps, proceeding as above, but never using more than a quantity which corresponds to 0.05 g. of fulminate; the solution obtained by treatment with thiosulphate is freed from antimony sulphide by filtering at once through a dry filter paper, and is then titrated as above.

The separation and determination of antimony sulphide and of potassium chlorate in cap compositions is effected by simply dissolving out the potassium chlorate.

Other nitro-compounds contained in cap compositions are detected by the methods applicable to the specific substances as severally described.

## C. STABILITY TESTS AND HEAT TESTS

In most countries it is prescribed that explosives shall be tested as regards their tendency to decompose on heating. Test papers prepared with potassium iodide and starch are almost universally used to indicate the evolution of nitrous acid evolved; in Germany, zinc iodide is used. The test is carried out as follows, according to the British specifications.

### I. GENERAL INSTRUCTIONS

*Apparatus required.*—1. A water-bath, consisting of a spherical glass or copper vessel, A (Fig. 75), of about 8 in. diameter and with an aperture of about 5 in.; the bath is filled to within  $\frac{1}{4}$  in. of the edge. It has a loose cover, B, of sheet copper, about 6 in. in diameter, and rests

<sup>1</sup> *Chem. News*, 1904, 89, 303.

on a tripod-stand, C, about 14 in. high, which is covered with a coarse iron wire gauze, E, and is surrounded by a screen of thin sheet tin or copper, D; an Argand burner, F, with glass chimney is placed below the screen. The cover B has four holes (Fig. 76*a*); No. 4 is for the regulator, No. 3 for the thermometer, and Nos. 1 and 2 for the test tubes containing the guncotton or other materials to be tested. The thermo-regulator is now dispensed with, as it is quite possible, to retain the temperature within  $1^{\circ}$  with the Argand burner. The Argand burner and tripod-stand may also be replaced by an ordinary paraffin burner. On the under side of the cover round the holes 1 and 2, three pieces of brass wire with slightly converging points are soldered (Fig. 76*b*); these

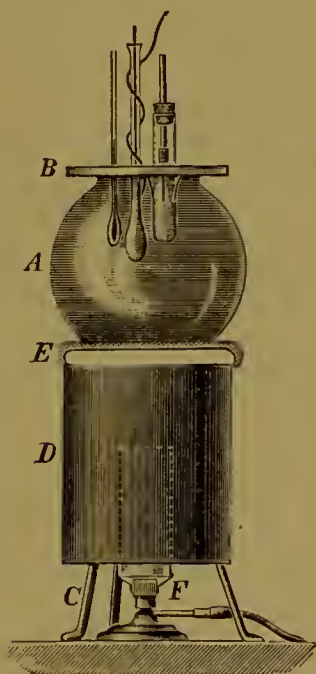


FIG. 75.

FIG. 76*a*.FIG. 76*b*.

FIG. 77.

act as springs, and allow the test tubes to be easily placed in position and removed.

2. Scheibler's or Page's thermo-regulator (cf. *ante*).
3. Two Leclanché cells.
4. A few yards of insulated copper wire.
5. Test tubes from  $5\frac{1}{4}$  to  $5\frac{1}{2}$  in. long, and of such diameter that they will hold from 20 to 22 c.c. of water when filled to a height of 5 in.
6. Rubber stoppers, fitting the test tubes and carrying an arrangement for holding the test paper, viz., a narrow glass tube passing through the centre of the stopper, drawn out so as to form a hook, or terminating in a platinum wire hook (Fig. 77).
7. A thermometer with range from  $30^{\circ}$  to  $212^{\circ}$  F.
8. A minute clock.

*Materials required.* 1. *Test Paper*.—The test paper is prepared as



follows:—45 grains (3 g.) of white maize starch (cornflour) previously washed with cold water, are added to  $8\frac{1}{2}$  oz. (250 c.c.) of distilled water, the mixture stirred, heated to boiling, and kept gently boiling for ten minutes; 15 grains (1 g.) of pure potassium iodide (*i.e.*, which has been recrystallised from alcohol) are dissolved in  $8\frac{1}{2}$  oz. (250 c.c.) of distilled water. The two solutions are thoroughly mixed and allowed to cool. Strips or sheets of white English filter paper, previously washed with distilled water and re-dried, are dipped into the solution thus prepared, and allowed to remain in it for not less than ten seconds; they are then allowed to drain and dry in a place free from laboratory fumes and dust. The upper and lower margins of the strips or sheets are cut off, and the paper preserved in well-stoppered or corked bottles, in the dark. When a paper is freshly prepared, and as long as it remains in good condition, a drop of dilute acetic acid, placed on the paper with a glass rod, produces no coloration. In process of time, however, the stronger the light to which the paper is exposed, the sooner a drop of the acid produces a brown or bluish coloration (a single hour of direct sunlight produces a marked effect), and whenever this is the case the paper should be rejected. On this account it is advisable not to prepare too much of the test paper at one time, but to prepare it fresh every month or so. The dimensions of the pieces of test paper used are about  $0.4 \times 0.8$  in. (10 mm.  $\times$  20 mm.).

2. *Standard Tint Paper*.—A solution of caramel in water is made up of such strength that when diluted one hundred times (10 c.c. made up to 1 litre) the tint of this diluted solution is equal to the tint produced by the Nessler test in 100 c.c. of water containing 0.000075 g. of ammonia or 0.000235 g. of ammonium chloride. With this caramel solution, lines are drawn on strips of white filter paper by means of a clean quill pen. The paper used must be carefully washed with distilled water in the first instance, to remove any traces of bleaching matter, and dried. When the marks thus produced are dry, the paper is cut into pieces of the same size as the test paper, in such a way that each piece has a brown line across it near the middle of its length, and only such strips are preserved in which the brown line has a breadth varying from  $\frac{1}{2}$  to 1 mm.

## II.—TESTING DYNAMITE, BLASTING GELATINE, AND OTHER EXPLOSIVES OF THE FIRST DIVISION OF THE NITRO-COMPOUND CLASS.

**Dynamite, etc.**—Nitroglycerine preparations from which the nitroglycerine can be extracted in the manner described below, must satisfy the following test, otherwise they will not be considered as manufactured with “thoroughly purified” nitroglycerine, within the terms of the

licence. This test, however, though at present looked upon as the most important as far as testing the purity of the nitroglycerine is concerned, is only one of several, which any given sample of nitroglycerine preparation has to satisfy, in order to establish its compliance with the definition in the licence. Although this test is at present accepted as regulating and defining the meaning of the terms "thoroughly purified," it may nevertheless be modified or superseded if, in the opinion of the Home Office such alteration may at any time be considered necessary.

*Apparatus required.*—A funnel of 2 in. diameter and a measuring cylinder divided into grains.

*Mode of Operation.*—About 300 to 400 grains (20 to 25 g.) of dynamite, finely divided, are placed in the funnel, which has previously been loosely plugged by some freshly ignited asbestos. The surface is smoothed by means of a flat-headed glass rod or stopper and some clean, washed and dried kieselguhr spread over it to the depth of about  $\frac{1}{8}$  in. Water is next carefully dropped from a wash-bottle upon this kieselguhr, and when the first portion has been soaked up, more is added. This is repeated until sufficient nitroglycerine has been collected in the graduated measure below. If any water should have passed through with the nitroglycerine it should be removed with a piece of blotting paper, and the nitroglycerine, if necessary, filtered through a dry filter paper.

*Application of the Test.*—The thermometer is fixed so as to be inserted through the lid of the water-bath (Fig. 75) into the water (which is to be steadily maintained at a temperature of  $160^{\circ}$  F.) to a depth of  $2\frac{3}{4}$  in. Fifty grains (3.24 g.) of the nitroglycerine to be tested are weighed into the test tube in such a way as not to soil the sides of the tube. A test paper is fixed on the hook of the glass rod (Fig. 77), so that when inserted into the tube it will be in a vertical position. A sufficient amount of a mixture of equal volumes of distilled water and glycerine to moisten the upper half of the paper is now applied to the upper edge of the test paper, by means of a camel's hair pencil, the cork carrying the rod and paper fixed into the test tube, and the position of the paper adjusted so that its lower edge is about half-way down the tube; the latter is then inserted through one of the perforations of the cover to such a depth that the lower margin of the moistened part of the paper is about  $\frac{5}{8}$  of an inch above the surface of the cover. The test is complete when the faint brown line, which after a time makes its appearance at the line of boundary between the dry and moist paper, equals in tint the brown line of the standard tint paper. The nitroglycerine under examination will not be considered as "thoroughly purified" within the terms of the licence unless the time necessary to produce the standard tint, as above described, is at least fifteen minutes

In works' laboratories where many tests are to be carried out in the course of the day, it is usual to employ larger water-baths and to measure out the nitroglycerine with a pipette instead of weighing it. The pipette holds 50 grains (3.240 g.) when filled to the mark, and the nitroglycerine is allowed to flow from it to the bottom of the test tube. The test paper must never be touched with the hand, since the slightest trace of impurity influences the paper. It is, therefore, advisable to keep a large piece of cork, on to which the paper is transferred from the bottle with a pair of forceps. A hole is made in the paper with a second pair of forceps, and the glass hook inserted into this hole. The glycerine mixture is then brought on to the paper with a glass rod; a very small drop is usually sufficient.

**Blasting Gelatine, Gelatine Dynamite, and Analogous Preparations.**—Fifty grains (3.240 g.) of blasting gelatine are intimately incorporated with 100 grains (6.480 g.) of French chalk. This can be readily effected by carefully working the two materials together with a wooden pestle in a wooden mortar. The French chalk should be of good commercial quality, and after being carefully washed with distilled water and dried in a water-oven, it should be exposed under a bell-jar to moist air until it has taken up about 0.5 per cent. of moisture. It should then be kept in a bottle for use; with ordinary care the limit of 0.5 per cent. of moisture can be maintained. The mixture is introduced gradually into a test tube of the dimensions prescribed above for the dynamite heat test, with the aid of gentle tapping upon the table between the introduction of successive portions of the mixture into the tube, so that when the tube contains all the mixture it shall be filled to the extent of  $1\frac{3}{4}$  in. of its height. The test paper is then inserted and the heat applied in the manner prescribed above for the dynamite heat test; the sample test shall withstand exposure to 160° F. for a period of ten minutes, before producing a discoloration of the test paper corresponding in tint to the standard colour test which is employed in the dynamite heat test.

### III.—TESTING GUNCOTTON, SCHULTZE GUNPOWDER, E. C. POWDER, AND OTHER EXPLOSIVES OF THE SECOND DIVISION OF THE NITRO-COMPOUND CLASS<sup>1</sup>

**Compressed Guncotton, Tonite, etc.**—Sufficient material to serve for two or more tests is removed from the centre of the cartridge by gentle scraping, and, if necessary, further reduced by rubbing between the fingers. The fine powder thus obtained is spread out in a thin layer upon a paper tray, 6 in. by  $4\frac{1}{2}$  in., which is then placed inside a water-oven, kept, as nearly as possible at 120° F. (49° C.).

<sup>1</sup> Cf. R. Robertson and B. J. Smart, *J. Soc. Chem. Ind.*, 1910, 29, 130.



The wire gauze shelves in the oven should be about 3 in. apart. The sample is allowed to remain for fifteen minutes in the oven, the door of which is left wide open. After the lapse of fifteen minutes, the tray is removed and exposed to the air of the room for two hours; at some time during this period the sample is rubbed upon the tray with the hand in order to reduce it to a fine and uniform state of subdivision.

*Application of the Test.*—The cover of the water-bath (Fig. 76) is fitted with the gas regulator which is inserted through the centre hole, No. 4, and the thermometer fixed in hole No. 3. The water in the bath is then heated to 170° F. (76°·6 C.) and the regulator set to maintain this temperature. Twenty grains (1·296 g.) of the sample to be tested are weighed out, placed in the test tube, and gently pressed down until the specimen occupies a space of as nearly as possible  $1\frac{5}{16}$  in. (3·3 cm.) in a test tube of the dimensions specified. A test paper is affixed to the hook of the glass rod or tube, and moistened by touching the upper edge with a drop of distilled water containing 50 per cent. of Price's glycerine (double distilled); the quantity of liquid used must be sufficient only to moisten about half of the paper. The cork carrying the rod and test paper is then fixed into the test tube, and the latter inserted into the bath to a depth of  $2\frac{1}{2}$  in. measured from the cover, the regulator and thermometer being inserted to the same depth. The test paper is to be kept near the top of the test tube, but clear of the cork, until the tube has been immersed for about five minutes. A ring of moisture will be deposited after about this interval upon the sides of the test tube a little above the cover of the bath; the glass rod must then be lowered until the lower margin of the moistened part is on a level with the bottom of the ring of moisture in the tube; the paper is then closely watched. The test is completed when a very faint brown coloration makes its appearance at the boundary line between the dry and moist parts of the paper. The interval of time between the first insertion of the tube containing the sample of guncotton in the water at 170° F. (76°·6 C.), and the first appearance of discoloration on the paper constitutes the test, and this interval of time must be *not less* than ten minutes or the sample will not be accepted as properly purified.

*Schultze Gunpowder, E. C. Powder, and Collodion Cotton.*—A sufficient quantity of the sample, without further mechanical division, is dried in the oven as above, and then exposed for two hours to the air. The test as directed above for compressed guncotton, etc., is then applied, the minimum duration of the test being the same, viz., ten minutes.

## IV.—HEAT TEST FOR CORDITE

(Also for similar Smokeless Powders.)

Pieces half an inch long are cut from one end of every stick selected for the test; in the case of the thicker cordites each piece so cut is further subdivided into about four portions (in the case of laminæ or cubes, a similar subdivision is effected). These cut pieces are then passed two or three times through a mill (a small cone mill), the first portion of material which passes through being rejected on account of the possible presence of foreign matter from the mill. The ground material is then placed on the top sieve of a nest of three sieves and sifted. That portion which passes through the top sieve but is stopped by the second is taken for the test. After each sample has been ground, the mill must be taken to pieces and carefully cleaned.

*Application of the Test.*—Twenty-five grains (1.620 g.) of the cordite are introduced into the tube with gentle tapping. A test paper is fixed in position as described above and moistened with glycerine. The water in the water-bath (Fig. 75) is retained at a temperature of 180° F. (82°·2 C.). The lower margin of the moistened portion of the paper should be approximately  $\frac{5}{8}$  inch above the surface of the lid. The brown line on the test paper should not appear within fifteen minutes.

The following method is prescribed in Germany for testing with zinc iodide-starch paper<sup>1</sup>:—One gram of nitrocellulose containing at most 0.5 per cent. of moisture, which is estimated in a separate sample by drying at 80°, is placed in a test tube 125 mm. high and 16 mm. wide, and gently tapped so as to form a layer from 30 to 40 mm. in depth; the test tube is closed by a cork fitted with a glass rod, to the lower end of which a piece of platinum wire, bent in the form of a hook, is attached, which serves to carry the test paper. The paper is 12 mm. wide, and 25 mm. long, and is suspended so that the lower edge is 20 mm. above the nitrocellulose; the lower half of the test paper is moistened with a 1 : 10 glycerine solution.

To carry out the test, the test tube is placed in a water-bath having a temperature of 80°, to a depth of 90 mm., and the time noted that is required for the appearance of a distinct blue or violet coloration at the boundary line of the dry and moistened portions of the paper. No coloration should be formed under ten minutes.

The zinc iodide-starch paper is prepared by grinding 4 g. of starch meal with a little water, and adding the turbid solution gradually to a boiling solution of 20 g. of zinc chloride in 100 c.c. of water. The solution is boiled until the starch is dissolved as completely as possible and the whole is almost clear, the evaporated water being replaced

<sup>1</sup> Cf. Post, *Chemisch-technische Analyse*, vol. ii., p. 938.

from time to time; this takes about two hours. The solution is then diluted, 2 g. of freshly prepared zinc iodide added, made up to a litre, and filtered; the filtrate forms an opalescent, almost perfectly clear liquid which remains colourless when kept in well-stoppered bottles in the dark; it should give no blue coloration when diluted with fifty times its volume of distilled water and acidified with dilute sulphuric acid (1:3). The test papers are prepared by dipping pieces of Swedish filter paper into the solution for one minute, and drying in an atmosphere free from acid fumes; the papers are then cut to size and kept in the dark in glass-stoppered bottles.

### OTHER HEAT TESTS

Guttman has proved<sup>1</sup> that the iodide test is inapplicable to many smokeless powders and a number of other explosives because these contain ingredients which mask the test, by combining with the liberated iodine. For this reason he proposed the use of a solution of diphenylamine in sulphuric acid and glycerine, instead of potassium iodide; this solution is prepared as follows:—0.100 g. of pure, crystallised diphenylamine is added to 50 c.c. of dilute sulphuric acid (1:4), and warmed on a water-bath to 50° to 55°; the diphenylamine melts at this temperature and dissolves in the dilute acid. After shaking several times, the flask is removed, cooled, and the solution preserved in a closed vessel in the dark; immediately before use, a small portion of this solution (about 0.5 c.c.) is mixed with an equal volume of chemically pure glycerine. Tubes, 12 cm. in length and 22 to 23 mm. in diameter, are used for the test, into which 6 g. of smokeless powder, or 3 g. of ungela-tinised nitrocellulose are introduced, the latter being pressed down until it occupies a height of about 25 mm. The test tube is closed as usual with a rubber stopper and glass rod, and strips of pure, thin filter paper 40 mm. long and 10 mm. wide are attached to the rods in such a way that the lower ends are suspended about 20 mm. above the powder. The two upper corners of the paper strip are moistened, by means of a glass rod, with a very small quantity of the diphenylamine solution, and the tube heated in the water-bath at a temperature of 80°. If the slightest trace of nitrous acid is evolved, the moistened corners become yellowish green, and as soon as a distinct blue line is observed at the margin of the wet and dry portions of the paper, the test is complete and the number of minutes required noted. On further heating, the corners are coloured, first pure blue, then slate blue, and finally a dirty yellow brown. The materials under examination must be quite dry, *i.e.*, on warming to 80° moisture must not be deposited on the glass in the upper part of the tube. If these conditions

<sup>1</sup> *Z. angew. Chem.*, 1897, **10**, 233, 267; *J. Soc. Chem. Ind.*, 1897, **16**, 283.



are adhered to, this method gives thoroughly reliable results; the test is not affected by the usual additions to powder or guncotton; only the presence of considerable quantities of diphenylamine in the powder renders the reaction somewhat indistinct. According to H. Ziegler,<sup>1</sup> this test has been in use for three years in Switzerland and gives very reliable indications as to the quality of the nitrocellulose; he has also pointed out that the keeping qualities of the indicator are improved by mixing the glycerine with the diphenylamine immediately before use, which is the rational procedure in view of the action of sulphuric acid on glycerine, and that it is advantageous to increase the quantity of the sample originally specified in the test.

In consequence of certain precautions which must be observed with this indicator, several criticisms and alterations, or similar tests, have been proposed. Thus Hoitsema<sup>2</sup> advocates heating the sample for a quarter of an hour and leading the gases evolved, by means of a current of carbon dioxide, through a solution of diphenylamine five times as concentrated as the above. Spica<sup>3</sup> has recommended metaphenylenediamine, which had been also experimented with by Guttman, but rejected on account of its extreme sensitiveness.

J. C. Thomas' method<sup>4</sup> consists in heating 3 g. of the sample in a tube with a glass stopper, suspended in an oil-bath at 100°, for eight hours each day until red-brown fumes are observed; a good nitrocellulose powder should resist this treatment for at least three days. But, H. C. Aspinwall<sup>5</sup> has reported cases in which twenty-one days were necessary for the appearance of visible fumes; the test is thus quite impracticable.

A similar test, in which, however, the powder is judged by the loss of weight, is in use in the Frankford Arsenal in Philadelphia. One to four whole pieces of the powder are heated for eight hours on a watch-glass at 115°, and this repeated for six days. The daily loss should not exceed 1 per cent. before six days have elapsed; after about eight days the rate of loss decreases; with unstable powders the loss is much greater. The bath is heated with a mixture of xylene and toluene.

Another test frequently used consists in heating to 135°. Two and a half grams of the sample are introduced into a tube 320 mm. long and having an internal diameter of 15 mm. and an external diameter of 18 mm., in which a strip of blue litmus paper is placed at a distance of 13 mm. from the explosive. The glass tube is lightly closed with a stopper, and the oil-bath covered with a lid in which are fixed a number of copper tubes closed at their lower ends. This bath is filled with *m*.-xylene and connected with a condenser; since the boiling point of the xylene is 135° the temperature is thus kept constant. The glass

<sup>1</sup> Private communication to Mr Guttman.

<sup>2</sup> *Z. angew. Chem.*, 1899, 12, 705.

<sup>3</sup> *Ibid.*, 1900, 13, 543.

<sup>4</sup> *Ibid.*, 1898, 11, 1027; *J. Soc. Chem. Ind.*, 1899, 18, 174.

<sup>5</sup> *J. Soc. Chem. Ind.*, 1902, 21, 687.

tubes are allowed to rest in the copper tubes and are thus heated. The time is noted at which the litmus paper becomes red, then the appearance of red fumes is observed, and finally the explosion of the sample. According to Sy,<sup>1</sup> the times prescribed by the American Government are as follows:—

	Reddening of Litmus Paper.	Red Fumes.	Explosion.
Nitrocellulose . . .	30 min.	45 min.	5 hours.
Nitrocellulose powder . .	1 hr. 15 min.	2 hr. 0 min.	5 hours.
Nitroglycerine powder . .	30 min.	45 min.	5 hours.

In order that reliable results may be obtained, it is necessary that the litmus paper be always uniform in quality and sensitiveness, and in America it is, therefore, obtained always from the same firm (Eimer & Amend, New York).

A similar test is in use in Austria and in Holland, in which the sample of explosive is enclosed in loosely stoppered weighing bottles, and heated for eight days at temperatures between 100° and 135°, the time being observed when red-brown fumes appear.

The Vieille test used in France is similar. An air oven is heated with glycerine, and the sample of 10 g. of explosive placed in a glass tube into the upper part of which a scroll of litmus paper is inserted. The heating is carried out at 110°. The time is noted at which the paper becomes violet, bluish red, rose-coloured, and distinctly red.

A quantitative stability test has been devised by W. Will,<sup>2</sup> which consists in heating 2.5 g. of dry nitrocellulose in a glass tube with a ground outlet tube, at 135° in an oil-bath, and passing a slow, regular current of pure, dry carbon dioxide through the tube. The resultant gases, containing nitrogen, are thereby continuously removed and are passed over ignited copper to reduce them to nitrogen. This is collected in a graduated U-tube, the volumes being read at stated intervals. A curve of the course of the decomposition is obtained by taking the times as ordinates and the quantities of nitrogen evolved as abscissæ. Well-purified nitrocelluloses give a perfectly regular curve.

Bergmann and Junk<sup>3</sup> have published a method worked out by them in the laboratories of the Prussian War Office which depends upon the liberation of nitric oxide. Glass tubes, to which are attached small absorption tubes half filled with water, are placed inside thick-walled brass tubes which dip into a bath of amyl alcohol. Two grams of nitrocellulose containing not more than 1 per cent. of moisture are introduced, the temperature maintained at 132°, and the tubes removed after two hours; in consequence of the cooling, the water rises in the

<sup>1</sup> *J. Amer. Chem. Soc.*, 1903, 25, 534.

<sup>2</sup> *Z. angew. Chem.*, 1901, 14, 746.

<sup>3</sup> *Z. angew. Chem.*, 1904, 17, 982; 1906, 19, 2105.

absorption tube and enters the heating tube, thereby soaking the explosive. The absorption tube is then rinsed out, the contents of the heating tube filtered, 1 c.c. of  $N/2$  potassium permanganate added to oxidise all lower oxides of nitrogen to nitric acid, and the nitrogen content of the filtrate determined by the Schultze-Tiemann (Schlösing) method. Good nitrocelluloses should not give more than 2.5 c.c. of nitric oxide.

A manometric test has been proposed by Obermüller, and a test depending on the measurement of the vapour tension by Dupré.

All the above stability tests are more or less open to criticism. The so-called heat tests are always, in a sense, empirical, and show chiefly whether an explosive contains impurities which are so unstable that they undergo decomposition more or less quickly. The quantity of these products may be very small, and an explosive may, notwithstanding their presence, be perfectly safe for storage, even although the heat test would indicate that insufficient care has been exercised in the purification. On the other hand, the tests which depend upon the heating to  $100^{\circ}$ - $135^{\circ}$  are well adapted to show the keeping properties of an explosive under abnormal conditions, but give no indication of the amount of care used in the manufacture. It is, therefore, advisable (as is done in many countries) to combine a heat test with a decomposition test, and in this respect it may be stated, in view of the methods officially adopted in various countries, that the most reliable results are obtained by a combination of the diphenylamine test with the decomposition test at  $135^{\circ}$ . Will's test is of great scientific value, but the costliness of the apparatus and the length of time (four hours) during which the experiment must be closely watched are disadvantageous; also, this test frequently gives indications of complete stability in cases in which the heat test is low.

The Bergmann-Junk test is identical in principle with Will's test but is only continued for two hours, instead of four as in Will's test. It has the advantage of greater simplicity of apparatus, but has the drawback that a special analysis is necessary, which almost counterbalances any saving of time otherwise attained. There is no objection to reducing the time of Will's test; if this be done the progress of the decomposition can be followed, which is not the case in Bergmann and Junk's method. For cases of special importance a combination of Will's test with a heat test gives the most reliable results. Guttmann in conjunction with G. W. Macdonald and W. Macnab has carried out a series of comparative tests with the various methods proposed,<sup>1</sup> and finds that the test at  $135^{\circ}$ , in a bath of amyl alcohol, as described above, is quick and reliable, the time required for the appearance of a distinct coloration on the tube being taken as the standard of

<sup>1</sup> Cf. *Twenty Years' Progress in Explosives*, 1909.



measurement; also, that the test compares favourably with all the other methods.

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## MATCHES AND FIREWORKS

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### A. MATCHES

THE following is a review of the materials used in the manufacture of matches.

#### I.—CLASSES OF WOOD AND THEIR SUBSTITUTES

Soft wood is employed which can be planed or sliced ("flaked") into splints. Match sticks are usually either square or round, according to whether they have been made by flaking or planing. The difference between these two kinds of splints is not only in form. Owing to the manner in which the round splints are made, a compression of the wood takes place, so that the sticks have a closer structure, and are less porous than the four-sided splints, made by flaking, which do not lose the structure and porosity of the wood from which they have been cut. The round splints, with their closer structure, are better suited for the manufacture of sulphur-coated matches, than for others. Sulphur-coated matches are covered at their lighting end with sulphur, and as this does not enter the pores of the wood, but remains only on the surface, it is unnecessary, for the manufacture of these matches, to choose a porous kind of wood with a loose structure. On the other hand, however, the wood must be such that it can easily be made into round splints. If, in place of sulphur, other substances are employed, such as wax, resin, fatty acids, such as stearin, or hydrocarbons, such as paraffin, then penetration of the wood by these materials, which on heating become liquid, is necessary. The wood used in such cases must be porous, and must remain so after its conversion into splints, so that it may absorb the above-mentioned substances. The grooved splints, and some of the round match sticks, now often seen are punched by upward-cutting dies from small wood blocks fed into the machine in an especial way.

In Great Britain sulphur is now scarcely ever, if at all, used for coating the splints, paraffin being employed instead.

### 1. Pine and Fir Wood.

In Great Britain, Canadian pine wood is at present the material chiefly used in the manufacture of match splints. For the production of round splints, the wood of young pine or fir trees is the best ; this wood must be dry, and if it is to be stored, should be kept in a well-aired place, protected from the rain and sun.

### 2. Aspen and Poplar Wood, etc.

Besides pine and fir wood, aspen, poplar, lime, and beech wood are used abroad. The wood of the aspen tree is exceedingly easy to flake and the splints obtained are very uniform. The strips of wood for match boxes are also made from the aspen tree, and on the same machine. According to Jettel,<sup>1</sup> aspen wood timbers with a length of 40 cm. are used ; the diameter should not be less than 20 cm., but preferably 25 to 60 cm. The demand for aspen wood for the manufacture of matches in Germany cannot be quite met, and a portion is, therefore, supplied from Russia ; the wood used in the United Kingdom for the "veneers" of which match boxes are made, is also supplied from Russia. It is probable that, for match splints also, aspen wood will eventually replace pine wood in this country.

### 3. Wax Matches or Vestas.

In the case of wax matches, the stem consists of a wick of twisted cotton threads, coated with wax, or more generally with mixtures of stearin, paraffin, and gum dammar or gum copal. Wax matches burn for a longer time than wooden matches.

## II.—SUBSTANCES USED TO IMPREGNATE THE SPLINTS

### 1. Means of Preventing the After-glow.

To prevent after-glow, and the falling off of the burnt heads, the splints are dipped in a solution of phosphoric acid and ammonium phosphate.

The solution, which is made up of 1.5 kg. of ammonium phosphate and 2 kg. of phosphoric acid in 200 litres of water, is placed in a wooden vat, and the splints are allowed to soak in this solution for about 10 minutes. The absorption can be accelerated by warming the solution by means of a steam pipe.

Alum also has been recommended for this purpose. Highly

<sup>1</sup> *Die Zündwarenfabrikation*, Hartleben's Verlag, Vienna, 1897.



hygroscopic substances, such as magnesium chloride, are, of course, unsuitable.

Technically pure chemicals are used.

## 2. Sulphur.

For occurrence, examination for purity, etc., see Vol. I., pp. 264 *et seq.*

Sulphur melts at  $113^{\circ}$  and forms a clear yellow liquid, which on further heating to above  $125^{\circ}$  becomes darker and at  $160^{\circ}$  is dark brown and viscous; at  $400^{\circ}$  it is again yellow and liquid, and commences to volatilise. If the sulphur becomes thick, it is too hot, and must be cooled down again before the splints can be dipped.

In the manufacture of matches the purity of sulphur is not material. Even should the sulphur *en masse* seem impure, the small quantity adhering to the splint always appears pure and is inflammable.

The variety of sulphur to be used generally depends on the source of supply and the price.

In the case of safety match compositions, only finely powdered roll-sulphur is used, and not flowers of sulphur.

*Differences between Powdered Sulphur and Flowers of Sulphur under the Microscope.* The powdered sulphur appears in the shape of more or less transparent crystals, while the flowers of sulphur appear as dark, cauliflower-shaped masses. In polarised light, between crossed nicols, the flowers of sulphur are optically inactive, while the broken, crystalline particles of the crushed sulphur appear light on a dark ground.

As previously stated, sulphur is scarcely ever used as a coating for the splints in this country, although it is an essential component of some match compositions, especially those used for safety matches.

## 3. Paraffin.

Details for the examination of paraffin are given in Vol. III. For the manufacture of matches, the more or less yellow and brown, soft, scaly paraffins are the most suitable. As paraffin is not a uniform substance, its melting point is not a constant. The price of paraffin is influenced by certain factors, which are largely dependent on the severity of the winter, as a cold winter favours the crystallisation of the scales of paraffin.

The most popular kinds are paraffin with a melting point of  $98^{\circ}$  to  $102^{\circ}$  F. (Scotch method of examination),  $101^{\circ}$  to  $105^{\circ}$  F. (American method), and  $38^{\circ}$  to  $39^{\circ}$  C. (German method): also a harder kind of paraffin, m.p.  $118^{\circ}$  to  $120^{\circ}$  F.,  $121^{\circ}$  to  $123^{\circ}$  F.,  $50^{\circ}$  to  $51^{\circ}$  C., is used by the Austrian makers, who make matches for export to the East.

There is still a great deal of uncertainty with regard to the way in which the English, Scotch, American, and German methods of examina-

tion are conducted. The results of the German and American methods agree well together, when the degrees Fahrenheit are converted into degrees Centigrade by the well-known formula  $F.-32:C.=9:5$ ; whereas after converting the English (or Scotch) degrees by the same formula, it is always necessary to add on  $2^{\circ}\text{C}$ . In this way,  $118^{\circ}$  to  $120^{\circ}\text{F}$ ., according to the English method, are not equal to  $48^{\circ}$  to  $49^{\circ}\text{C}$ . German method, but are equal to  $50^{\circ}$  to  $51^{\circ}\text{C}$ .

The ignorance of this difference in the methods is often taken advantage of by dealers, as paraffin is sold according to its melting point, and the German test (also known as the "Halle Test," *cf.* Vol. III., "Candle Manufacture" and "Lubricating Oils") gives higher results. The *Verein für Materialientechner* officially recognises the Schorkoff method, which has been in use in the lignite industry for many years (*cf.* Vol. III., "Lubricating Oils").

The only test required in the match industry, is to take the melting point of the paraffin before use.

In impregnating the splints with paraffinwax, the molten paraffin is heated to such a point that a match stick "boils" when thrown into it. As the vapour of paraffin wax is unpleasant, the paraffin bath should be fitted with a powerful air draught.

#### 4. Stearin.

Stearin is obtained by saponifying tallow, decomposing the soap with acid, and pressing the solid residue. It melts at  $70^{\circ}$ , and forms a waxy, crystalline mass. It was used at one time, with the addition of a little resin (colophony), to prepare the wood for matches "de luxe." The addition of resin causes the flame to smoke strongly. For use in the match industry, it is not necessary to use the hardest and whitest sorts of stearin; on the contrary, the softer kinds seem to serve the purpose better. For wood matches, stearin is now replaced by paraffin, but it is used, together with gum copal or dammar, for wax match stems.

The Schorkoff melting point method, mentioned above, is used for the examination of stearin.

#### 5. Wax.

Wax, when first obtained, forms a yellow mass: this, if melted and allowed to run out into cold water, forms thin strips, which are slowly bleached by the action of the air. In the bleached condition, wax is a white, nearly odourless and tasteless mass, with a splintery fracture; at  $30^{\circ}$  it can be kneaded, and it melts at  $65^{\circ}$  to  $68^{\circ}$ .

Wax is occasionally used in the manufacture of wax matches, but in this country stearin, with or without paraffin, is generally substituted partly or entirely. Cotton threads on bobbins are passed through a

ring, so as to form one single thread, which is then passed through a trough containing the molten wax mixture. This thread is then passed through a wire-drawing plate, which gives it an exactly cylindrical shape and a smooth surface. The wax is not used pure, but mixed with stearin or paraffin; a good mixture generally contains 10 to 15 per cent. of wax. In the case of wax matches which are required for use in tropical climates, it is usual to add a small quantity of Carnaüba wax, which prevents the matches from becoming soft and sticking together.

### 6. Resin.

The dried resin of the coniferæ is used in match compositions, or for mixing with the stearin; Venice turpentine is the best.

## III.—MATERIALS FOR MATCH COMPOSITIONS

### A. COMBUSTIBLE SUBSTANCES

**1. White or Yellow Phosphorus.**—This is, when fresh, almost colourless and transparent, looks like wax, and has a waxy consistency; at a low temperature it is brittle. Sp. gr. 1.83. Melting point  $44^{\circ}$ . Boiling point  $290^{\circ}$ . It is almost insoluble in water and alcohol, soluble with difficulty in ether and fatty ethereal oils, easily soluble in carbon bisulphide, chloroform, benzene, and sulphur chloride ( $S_2Cl_2$ ). Fresh phosphorus, when exposed to the air, shines brightly in a dark room; at the same time, ozone and ammonium nitrite are formed. Friction, or warming to  $60^{\circ}$  in the air, will cause phosphorus to burn with a bright, yellowish white flame, to phosphorus pentoxide ( $P_4O_{10}$ ). Phosphorus is a deadly poison, 0.1 to 0.2 g. causing death; constant inhalation of the "fume" causes phosphorus necrosis,<sup>1</sup> which is liable to attack chiefly the jaws and carious teeth of workers in match factories, where white phosphorus is used.

*Examination of Commercial Yellow or White Phosphorus.* The impurities contained in phosphorus are derived chiefly from the sulphuric acid used in the manufacture, and can best be detected by analytical methods. Pure phosphorus has, besides the properties already mentioned, a certain pliability, which it loses as soon as a small trace of sulphur is present. To test for sulphur, a fragment of the phosphorus is dissolved in nitric acid, and the solution, which now contains the phosphorus as phosphoric acid, tested with a solution of barium nitrate; a white precipitate, insoluble in nitric acid, shows the presence of sulphuric acid. Another portion of the solution is diluted, nearly neutralised with alkali, and treated with sulphuretted hydrogen; if there was arsenic present in the nitric acid solution, it would be

<sup>1</sup> Cf. Muspratt's *Technische Chemie*, vol. x.



present as arsenic acid, which on heating to  $60^{\circ}$  to  $80^{\circ}$  with sulphuretted hydrogen, would give a yellow precipitate of arsenious sulphide. If iron be present, a precipitate of Prussian blue is obtained, on the addition of a few drops of a solution of potassium ferrocyanide.

**2. Dark red Amorphous Phosphorus** is formed by the continued heating of white phosphorus at  $240^{\circ}$  to  $250^{\circ}$  in a current of some indifferent gas, such as carbon dioxide. At a still higher temperature the red modification changes back again into the white. Ordinary red phosphorus is a dark red, partly amorphous powder, with a sp. gr. of 2.1. It does not shine in the dark, oxidises only slowly in the air, and only commences to burn when heated to above  $360^{\circ}$ . Friction does not cause it to catch fire, but it explodes when rubbed together with potassium chlorate or with peroxides.

It is used chiefly for the preparation of the striking surfaces on safety match boxes, and is also occasionally employed in the manufacture of "strike-anywhere" match compositions.

Pure red phosphorus is not poisonous, and can neither be dissolved nor oxidised in the system; commercial red phosphorus can, however, act as a poison, as it frequently contains a small quantity of the white modification. R. Fresenius and E. Luck found the following substances in a sample of commercial amorphous phosphorus:—

Red phosphorus	.	.	.	92.63	per cent.
White phosphorus	.	.	.	0.56	„
Phosphorous acid	.	.	.	1.302	„
Phosphoric acid	.	.	.	0.880	„
Water and impurities.	.	.	.	4.662	„

Although the presence of a small quantity of white phosphorus is not in itself detrimental in match making, it has been assumed to be the cause of a slow oxidation to phosphorous and phosphoric acids, which on account of their acid and hygroscopic properties, act on the other substances present.<sup>1</sup> This supposition is, however, unnecessary, for red phosphorus, which has been purified with the utmost care, becomes oxidised after long contact with the air, and contains under these conditions considerable quantities of phosphorus acids. In a compact state, in which the oxidisable surface of the phosphorus is comparatively small, as in the case of a match composition, which is often covered by a slight coating of varnish, the possibility of oxidation is considerably decreased. A more or less moist appearance of the phosphorus indicates the presence of acids. Factories do not generally trouble about any special examination or purification, although in 1909 it was proposed to use "neutral amorphous phosphorus," obtained

<sup>1</sup> Cf. Fresenius and Luck, *Z. anal. Chem.*, 1872, **11**, 63.

from the ordinary product by purification methods.<sup>1</sup> The phosphorus acids are determined quantitatively by extracting a weighed quantity (10 g.) on a filter with warm water, until the filtrate no longer reacts acid. A definite portion of the filtrate is oxidised by continued evaporation with nitric acid, and the total phosphoric acid then precipitated in the usual way with magnesium ammonium chloride. The phosphorous acid is estimated with mercuric chloride<sup>2</sup> in another portion of the filtrate. To estimate the percentages of white and red phosphorus present, R. Fresenius and E. Luck<sup>3</sup> oxidise the phosphorus, after it has been washed free from acids with warm water, with fuming nitric acid to phosphoric acid, and estimate the amount of phosphorus in this as magnesium ammonium phosphate. The quantity of red phosphorus is similarly estimated in another portion of the sample, after extracting the white modification with carbon bisulphide. The difference between these two quantities gives the amount of white phosphorus present.

As there are certain difficulties in carrying out this estimation, match manufacturers are generally satisfied with the qualitative test. For this purpose, the phosphorus, after the removal of the phosphorus acids, is first treated with absolute alcohol, to eliminate any water present, and then with carbon bisulphide; this solution is then carefully evaporated, and the presence of white phosphorus tested for by its luminosity in a dark room. Or, according to Nicklés,<sup>4</sup> the phosphorus is shaken with a solution of calcium chloride of sp. gr. 1.95; on standing, the white modification (sp. gr. 1.83) rises to the surface. This method, however, is not very accurate.

The German official method, worked out by Siemens, is as follows<sup>5</sup>:—Three grams of phosphorus are dried, and boiled for half an hour on a steam-bath, under a reflux condenser, with 150 c.c. of benzene and filtered. One c.c. of this solution is added to 1 c.c. of a solution of ammoniacal silver nitrate, which is made by dissolving 1.7 g. of silver nitrate in 100 c.c. of ammonia of sp. gr. 0.992. If, after shaking and allowing to stand, no change, or only a yellow coloration of the aqueous solution takes place, white phosphorus is absent. But if, after these operations have been carried out, the aqueous liquid be coloured red or brown, or contain a black or brownish black precipitate, white phosphorus is present. The colour of the aqueous solution should be judged directly after shaking and allowing to stand, and not after prolonged standing.

**3. Light red Amorphous Phosphorus** can be prepared, according

<sup>1</sup> Caussemille Jeune et Cie. and Roche et Cie., Fr. Pat. 404337, 23rd June 1909.

<sup>2</sup> *Pogg. Ann.*, 1860, 110, 529.

<sup>3</sup> *Z. anal. Chem.*, 1872, 11, 63.

<sup>4</sup> Wurtz, *Dictionnaire de Chimie*, Paris, 1876, II., 2, 995.

<sup>5</sup> *Z. angew. Chem.*, 1907, 20, 233, 523; Erlass des Reichskanzlers, 25th December 1906.

to Schenck,<sup>1</sup> by boiling a 10 per cent. solution of white phosphorus in phosphorus tribromide. Owing to its more finely divided condition, it is rather more active than the dark red modification; it contains, besides unchanged white phosphorus, a moderate quantity of phosphorus bromide, or of phosphorous acid, which can only be partially removed by boiling with water. White phosphorus can be eliminated by boiling with carbon bisulphide. The final product contains only 90 per cent. of phosphorus. This modification can be converted into the dark red form by continued heating at 300° in a current of carbon dioxide. The light red form is also non-poisonous, and is used in compositions for "strike-anywhere" matches.

Schenck determines the phosphorus, by heating a weighed quantity with water together with bromine, contained in a small tube, in a sealed tube, for two or three hours in a steam-bath at 100°; the oxidised phosphorus is weighed as magnesium pyrophosphate.

**4. Phosphorus sesquisulphide** ( $P_4S_3$ ).—This compound, first prepared by G. Lemoine, is formed by slowly heating the calculated quantities of phosphorus and sulphur in a current of carbon dioxide at 330°; a small excess of sulphur is used. At a higher temperature, white phosphorus is re-formed (Mai and Schaffer).<sup>2</sup> By sublimation at 260°, regular crystals are obtained, but on crystallisation from carbon bisulphide, rhombic prisms result. The compound melts at 160° to a reddish liquid. It is soluble in carbon bisulphide, phosphorus trichloride, and in aqueous solutions of sodium and potassium sulphides. Alkalis decompose it. Commercial phosphorus sesquisulphide ignites in air at 98° to 99°. Cold water has scarcely any action, but water at 100° decomposes it into sulphuretted hydrogen and phosphorous acid. The pure product keeps for a long time in well-stoppered bottles; the commercial products are less stable, and their decomposition can be recognised by the smell of the evolved sulphuretted hydrogen. The greater the impurity of the product, the more pronounced is the odour. This decomposition is caused by the action of the oxygen of the air:—



Phosphorus sesquisulphide was officially introduced into France by Sevène and Cahen,<sup>3</sup> for the manufacture of "strike-anywhere" matches, free from white phosphorus. The less pure varieties may contain small quantities of white phosphorus, for which careful tests must be made.

The examination is carried out firstly by the smell (the odour of phosphorus), and then by Mitscherlich's test (*cf.* detection of phosphorus in match-heads, p. 564), or by Schenck and Scharff's process. These methods are very exact, and allow of the detection of extremely small traces. In examining and judging matches, such minute traces of

<sup>1</sup> *Ber.*, 1903, 36, 979.

<sup>2</sup> *Ibid.*, 1903, 36, 870.

<sup>3</sup> *Ger. Pat.* 101736.



phosphorus must not be taken into account; in Germany certain less delicate official tests are accordingly adopted (*cf.* p. 566).

**5. Lead thiosulphate** is now used for the preparation of match compositions, which ignite on any surface. It is made by treating a solution of sugar of lead with sodium thiosulphate; it is a pure white, inodorous and tasteless powder, insoluble in water and not hygroscopic. It should be kept in well-closed bottles.

Twelve kilograms of acetate of lead will yield, when treated with 5 kg. of sodium thiosulphate, about  $9\frac{1}{2}$  kg. to  $9\frac{3}{4}$  kg. of lead thiosulphate. When pure, a small sample, shaken with water, should show no soluble matter.

**6. Antimony trisulphide** is used partly for match compositions, but is mainly used on the striking surface of safety match boxes. It can be obtained finely ground and with a purity of 99 per cent. Tests for purity are not necessary.

**7. Other Substances.**—A few other substances have been recommended for match compositions, such as persulphocyanic acid,<sup>1</sup> ferrocyanogen compounds, potassium xanthate, thiocyanates, "sulfo-cuprobaryum polythionat,"<sup>2</sup> and "thiophosphit" or "sulfophosphit."<sup>3</sup>

#### B. SUBSTANCES WHICH SUPPLY OXYGEN

**1. Minium,  $Pb_3O_4$ ,** is made by the continued heating of lead oxide or white lead in the air at  $300^\circ$  to  $400^\circ$ ; it has a bright red colour. The use of minium is solely dependent on the percentage of oxygen which it contains, and, therefore, only the purest product, containing not more than 1 per cent. of foreign matter, should be used. This is tested for by dissolving 1 g. in a mixture of 2.5 g. of nitric acid (sp. gr. 1.15), 3 g. to 4 g. of water, and 0.5 g. of oxalic acid, and filtering.<sup>4</sup>

**2. Lead peroxide in admixture with Lead nitrate.**—This "mixture" is prepared by treating minium with nitric acid of sp. gr. 1.384. A moderate amount of heat is liberated. Minium, which consists of a mixture of lead oxide and peroxide, gives up the lead oxide to the nitric acid to form lead nitrate, and the peroxide remains unchanged. An excess of nitric acid is to be avoided, as it not only acts on the binding substance in the match composition, but also makes the phosphorus inactive, by oxidising it to phosphoric acid. Moreover, it gives the mixture a thin consistency, whereas if the correct quantity of acid is used, the product is stiff and pasty. A badly treated mixture contains too much lead nitrate, which causes the match head to sweat, thereby producing a bad ignition and giving an unsightly appearance

<sup>1</sup> J. Craveri, Eng. Pats. 18563 and 27520, 1897.

<sup>2</sup> Ger. Pat. 157424.

<sup>3</sup> Ger. Pat. 153188.

<sup>4</sup> *Cf.* Bujard, *Leitfaden der Pyrotechnik.*, 1899, p. 88.

to the match head. The product must also be free from lead chloride and lead sulphate, which will be the case if pure minium and pure nitric acid are used.

3. **Lead peroxide** is made by treating minium with pure nitric acid, free from hydrochloric and sulphuric acids, and then extracting the lead nitrate thus formed. The percentage of lead peroxide can be estimated by Ebell's method.<sup>1</sup> Half a gram of lead peroxide is weighed into a small flask, mixed with water to a thin paste, a large excess of concentrated hydrochloric acid added, and the flask closed with a well-fitting rubber stopper provided with a delivery tube, which is led into a Varrentrapp's bulb apparatus, containing a solution of potassium iodide. The flask is then gently warmed, with frequent shaking. The lead peroxide dissolves to the tetrachloride ( $\text{PbCl}_4$ ), of which only traces reach the potassium iodide solution. The small flask is next cooled by placing it in cold water, when the solution of potassium iodide flows back into it and liberates iodine. After dilution with water to 300 c.c. in a beaker, the liberated iodine is titrated with sodium thiosulphate. One c.c. *N*/10 thiosulphate is equivalent to 0.01196 g.  $\text{PbO}_2$ .

An alternative method is to treat the lead peroxide with a measured volume of hydrogen peroxide, which has been acidified with nitric acid. The following reaction takes place:—



The undecomposed hydrogen peroxide can be determined by titration with potassium permanganate solution.

*Example.*—Two c.c. of hydrogen peroxide required 35.1 c.c. of *N*/10 permanganate; 4 c.c. of hydrogen peroxide were then acidified with nitric acid diluted with 50 c.c. of water, and digested with 0.5 g. of powdered lead peroxide in the cold. When the lead peroxide had passed completely into solution, the liquid was titrated with *N*/10 permanganate, 30 c.c. being required.

Four c.c. hydrogen peroxide required 70.2 c.c. permanganate.

Four c.c. hydrogen peroxide, after treatment with lead peroxide, required 30 c.c. permanganate.

Difference due to lead peroxide, 40.2 c.c. permanganate, corresponding to 96.02 per cent. lead peroxide.

4. **Lead nitrate** can most easily be obtained in match factories, by allowing the wash-waters, obtained in the preparation of lead peroxide, to crystallise.

5. **Manganese peroxide.**—The tests are fully described in Vol. I., pp. 476 *et seq.* In the match industry, great weight is laid on the purity of this substance and the degree of fineness to which it has been ground. It is seldom used for phosphorus compositions, but is

<sup>1</sup> *Rep. anal. Chem.*, 1886, 6, 141.

employed for safety and non-poisonous, "strike-anywhere" match pastes, and also on the striking surfaces.

**6. Potassium chlorate.**—This is examined as described in Vol. I., p. 517. It is the most powerful oxidising agent used in the match industry; it is not recommended to substitute it by the very hygroscopic sodium chlorate.

**7. Potassium nitrate.**—For the examination, see Vol. I., pp. 306 *et seq.* Only the purest saltpetre should be used. It is especially important that it should be free from chlorides, as it must not deliquesce.

**8. Potassium bichromate.**—For tests *cf.* this Vol., p. 364. It is used in the manufacture of safety matches, also in very small quantities in the compositions of red phosphorus matches.

**9. Barium nitrate, Strontium nitrate.**—These substances are used in pyrotechny.

**10. Calcium orthoplumbate,**  $\text{Ca}_2\text{PbO}_4$ , is a heavy, yellowish red powder, first prepared by Kassner,<sup>1</sup> and was recommended as a substitute for lead peroxide and lead nitrate, in the manufacture of non-poisonous, "strike-anywhere," phosphorus matches. Schwiening's<sup>2</sup> composition, which was purchased by the German Government, and is used by match makers, owing to the prohibition of the use of white phosphorus, contains calcium orthoplumbate, together with potassium chlorate, amorphous phosphorus, friction material, binding and colouring substances. The matches made with it are called "Triumph" matches.

The calcium plumbate appears to act as a negative catalysing agent on the explosive mixture of potassium chlorate and phosphorus, retarding the explosion, so that only inflammation occurs.

#### C. SUBSTANCES WHICH INCREASE FRICTION; AND INERT SUBSTANCES, OR FILLING MATERIALS

- |                         |                     |
|-------------------------|---------------------|
| 1. Powdered glass.      | 7. Siliceous marl.  |
| 2. Pumice stone.        | 8. Kieselguhr.      |
| 3. Sand.                | 9. Powdered quartz. |
| 4. Chalk.               | 10. Brown umber.    |
| 5. Plaster of Paris.    | 11. Venetian red.   |
| 6. Pulverised asbestos. | 12. Zinc oxide.     |

These serve, on the one hand, to increase the friction, and on the other to retard the explosion on igniting the match head, so that the flame has time to act on the other materials, sulphur, paraffin, etc., which propagate the combustion. The use of chalk as a filling material is now rare. Zinc oxide is employed chiefly in the compositions of matches containing phosphorus sesquisulphide, red phosphorus, and the like.

<sup>1</sup> *Dingl. polyt. J.*, 1889, 274, 185; *Chem. Zeit.*, 1903, 27, 1130.

<sup>2</sup> Ger. Pat. 86203.



These substances can all be obtained in the required degree of purity. The siliceous marl contains 80 to 92 per cent. of silica, as well as alkaline earths and iron.

## D. BINDING SUBSTANCES

### I. Glue.

#### I.—THE COMPOSITION AND MANUFACTURE OF GLUE

The collagens, or substances which yield glue by heating with water in a steam-heated boiler, are such portions of vertebrate animals as the connective tissue, and the intercellular substance of the sinews, ligaments, bones, and dentine. Chemically, there are two different kinds of glue: bone glue (glutin), and glue from the cartilage (chondrin).

1. *Glutin*, the main constituent of commercial glue, having the formula  $C_{13}H_{20}N_4O_5$ , swells up in water, without dissolving, becomes liquid on heating, and gelatinises on cooling. Glutin is soluble in acids and alkalis at the ordinary temperature. If glutin is boiled continuously with water, it becomes peptonised (glue peptone), and loses its solidifying property, that is to say, it does not gelatinise on cooling. It is not precipitated by acetic acid, ferrocyanide of potassium, or nitric acid (difference from the true albuminoids). Glutin is thrown out of solution by most varieties of tannic acid, and on this fact the quantitative estimation of these acids with hide-powder is based.

2. *Chondrin* is obtained by boiling the cartilage with water; the resulting opalescent liquid gelatinises on cooling. It can be precipitated by dilute mineral acids, but redissolves in excess. Some chemists regard chondrin as a mixture of ordinary glue and mucin.

Commercial glue is divided into two classes, according to the raw products from which it is made, viz.: *skin-glue* and *bone-glue*.

#### II.—PROPERTIES AND EXAMINATION OF GLUE

The principal uses are as an adhesive, and as a binding material. Good glue should be very hard and not easily breakable; when struck it should give a loud, sharp sound. It should be clear and transparent, with a pale colour; this last property may, however, give rise to mistakes, as the so-called benzine glues, although thin and pale-coloured, are, as a rule, of bad quality. When placed in cold water, good glue should only swell, and take up a large quantity of water, without dissolving; the water should not smell, and should not show any appreciable cloudiness. Good skin-glue dissolves completely at 50°. Numerous methods are in use to test the quality of glue. Lipowitz estimates the

bearing power of a gelatinised glue solution of definite concentration, and at a definite temperature, whereas Weidenbusch estimates the binding power itself.

*Liquid Glue.* This can be obtained by treating 100 parts of glue with 140 parts of water and 16 parts of nitric acid; it still retains the adhesive power of the glue used in its production, but does not gelatinise. This glue, and also liquid glue made with acetic acid, will not serve for the manufacture of match compositions, and it is advisable that these substances should not be used at all for the purpose.

A good glue, suitable for match compositions, should be yellow to light brown in colour, not dark, and should not break easily, must not rapidly absorb moisture from the air, and should be in the form of flat cakes. The fracture must be glassy; a splintery fracture shows incomplete melting of sinewy portions. The glue should only swell in cold water after forty-eight hours, and should not have become liquid; this swollen glue becomes liquid at  $48^{\circ}$  to  $50^{\circ}$ ; boiling or continued heating causes the glue to lose its binding power.

*Examination.* A rough practical test for glue is to examine it with the tongue. If it taste salt or acid, it is unsuitable for the manufacture of matches. The same applies when it has an unpleasant taste after having been breathed upon for some time. Another test is as follows:—An exactly weighed quantity of dry glue is allowed to remain for twenty-four hours in cold water, then allowed to dry and weighed again. The nearer the final weight approaches to the original, the better is the sample.

The requirements of a glue as regards its properties vary with the purpose for which it is to be used. In some cases it is important that the glue shall be as free as possible from smell, in others, neutrality is the chief consideration; in others again, the drying properties are of importance, whilst finally the buyer often lays chief stress upon the binding power of the glue. As the determination of the binding power is difficult, Kissling<sup>1</sup> devised the following scheme for testing glue, which is not too complicated, and permits of the determination of the value of a sample on the basis of a series of easily conducted experiments.

### III.—KISSLING'S SCHEME FOR TESTING GLUE

1. *Determination of Moisture.* A certain quantity is detached from the slab of glue with the aid of a coarse wood rasp, and 2 to 3 g. are quickly weighed out on to a large watch-glass, and dried to constant weight in an air-oven at  $110^{\circ}$  to  $115^{\circ}$ . It is absolutely necessary to carry out the drying with finely powdered glue, for the moisture cannot

<sup>1</sup> *Chem. Zeit.*, 1887, **11**, 691, 719; see also Post, *Chem. techn. Analyse*, 1908, vol. ii., p. 858.

be completely expelled at the above temperature from slightly larger particles, and it does not appear advisable to resort to a higher temperature. It should be observed that powdered glue loses very perceptibly in weight, if allowed to stand in the laboratory at the ordinary temperature for some time.

2. *Determination of Ash.* For the determination of the ash it is convenient to use the same sample of glue that was taken for the moisture determination. It is incinerated in a covered platinum crucible, the full heat of a Bunsen burner being at once applied. The traces of mineral matter which are lost in this shortened method may be neglected without danger, since only great differences in the quantity of ash need be taken into account. The last particles of carbon, which are somewhat difficult to remove, are best burnt by repeatedly allowing to cool, moistening, and igniting the contents of the crucible.

3. *Qualitative Examination of the Ash.* The nature of the ash generally gives reliable indications as to whether the glue was derived from bone or from hide. The ash of bone-glue melts at the temperature of the Bunsen burner, its aqueous solution generally reacts neutral, and its solution in nitric acid gives the reactions for phosphoric and hydrochloric acids. If the ash has been very strongly ignited, deposits of alkaline chlorides are found on the inside of the crucible cover and sometimes on the edge of the crucible. The ash of skin- or hide-glue contains a large proportion of lime and remains, therefore, unmelted. It reacts strongly alkaline and is generally free from phosphates and chlorides.

4. *Determination of Alkalinity.* To 2 g. of glue, dissolved in 18 g. of water, are added 40 g. of 99 per cent. alcohol; after brisk agitation, the mixture is filtered and titrated with  $N/10$  hydrochloric acid, phenolphthalein being employed as the indicator.

5. *Free Mineral Acid* is determined by titrating a 10 per cent. solution of the glue in water with aqueous sodium hydroxide solution, successive portions of the liquid being spotted on to neutral litmus paper. The quantity of alkali to be added each time before the spotting must correspond to 0.005 g.  $H_2SO_4$ . During the titration, the glue solutions are warmed to about  $30^\circ$  to  $40^\circ$ .

6. *Determination of the free and combined volatile Acids.* Thirty grams of the glue are covered with 80 g. of water in a round-bottomed flask and placed aside for a few hours to allow the glue to swell. An arrangement is then fitted up which permits of the removal of the volatile acids by steam distillation, the flask being conveniently placed in a vessel containing boiling water, in order to avoid the condensation of any considerable quantity of steam. As soon as the distillate no longer has an acid reaction, the distillation is stopped, and the quantity of acid is determined by titration. To liberate the combined volatile acids, the contents of the flask are next acidified with concentrated



sulphuric acid, and distilled again in a similar manner. In some instances the distillate contains considerable quantities of sulphurous acid, so that it is advisable to distil into a known quantity of standard alkali. The sulphurous acid can be converted into sulphuric acid by the addition of bromine, and then determined gravimetrically.

7. *Determination of the Drying Properties.* The solution of glue, freed from volatile acids, is diluted with water to a weight of 150 g. and again heated to the temperature of boiling water with an upright tube to prevent loss by evaporation. Ten c.c. are then withdrawn by a pipette on to the middle of a watch-glass of about 10 cm. diameter, in such a way that no glue is present on the glass outside the circular disc of jelly, the centre of which must coincide with that of the glass. The watch-glass is placed in a horizontal position before the addition of the glue; it should be allowed to remain in a place as free as possible from dust and draughts, and where the temperature is not liable to fluctuate greatly. The alterations of the glue are then observed for a few days. According to the drying properties of the glue, the jelly dries more or less quickly from the edge to the centre, and from the size of the patch which still remains soft after a certain time, a fairly reliable conclusion can be drawn as to the drying properties of the sample. As the process of drying is greatly influenced by the degree of moisture and temperature of the air, and as it is very difficult to keep these constant, it is advisable always to carry out comparative determinations. It is, therefore, advantageous to compare the glue under examination with two samples which have been previously tested, one of good, and the other of inferior drying properties, the three being treated identically, as above.

8. *Determination of Foreign Matter.* In order that the method of testing may not be unnecessarily complicated, Kissling recommends only an approximate quantitative determination of the total quantity of those substances which are deposited when the glue solution is sufficiently diluted. As the separation of these substances by filtration is troublesome and slow, even after partial separation by decantation, Kissling makes approximate determinations of the volume of the solid deposit, since the estimation is only comparative. The glue solution referred to in (7)—that is to say, 150 c.c. less 10 c.c.—is diluted with hot water, allowed to cool, introduced into a cylinder of 1000 c.c. capacity, graduated in c.c., filled up to the mark, mixed, and allowed to stand. The volume of the solid deposit, after twenty-four hours, forms a measure of the quantity of insoluble "foreign matter" in the glue. This is generally very small, but in some cases considerable. Such substances decrease the binding quality of the glue, when they consist to a great extent of organic matter, as Kissling found in a number of cases.

9. *The Odour.* This feature is of especial importance, as it gives

indications concerning the durability of glue, and its tendency to decompose. The smell of glue varies greatly according to the quality. Usually, hide-glues are in this respect superior to bone-glues. With some kinds of glue, the smell of the cold slabs is very slight, whereas the hot jellies have a very unpleasant smell. In such cases the glued surface, after drying, has a much more unpleasant smell than the cold slab. In his published results, Kissling, therefore, gives indications of the smell, both of the dry glue and of the hot jelly. Obviously, it is only possible to judge the odour accurately after carrying out a long series of investigations of glues.

As regards the practical value of this scheme of testing, Kissling remarks that in general a satisfactory agreement has been found between the results of practical experience and those of his investigations. The amount of acidity determines the suitability of a glue for some purposes. The quantitative estimations of water and ash are generally of minor importance; and the same, as a rule, may be affirmed of the determination of fat, methods for which are described in the next sub-section. Hide-glues show a superiority over bone-glues, but it must be emphasised that the manufacture of bone-glue has undergone such improvements that its relative value in comparison with hide-glue has greatly increased. The best bone-glues now compare approximately with medium skin-glues.

In a subsequent publication, Kissling<sup>1</sup> emphasises the fact that all forms of apparatus devised for the purpose of directly measuring the binding power,<sup>2</sup> the first requirement in the testing of glues, fail to give even approximately concordant results under identical conditions of experiment. This is, at all events, his experience with apparatus devised by himself for this purpose (*loc. cit.*), and for this reason he prefers the determination of the drying properties of glue. In a later paper<sup>3</sup> he strongly advocates, and describes an apparatus for, ascertaining the melting point of the glue jellies.

The following results (see Table, page 540) are quoted, with some additions, from a paper by E. G. Clayton,<sup>4</sup> on the Technical Examination of Glue, based on investigations of a number of samples of British and foreign origin.

The main conclusions in the paper are as follow:—Colour is of limited value as an indication of quality, and too much importance is often attached to it. Some dark-tinted glues may be better in quality than comparatively pale samples. Air-bubbles should be few, or better, absent. The odour of samples should be inoffensive. Good glue should not deteriorate quickly on exposure. Physical tests usually

<sup>1</sup> *Chem. Zeit.*, 1889, 13, 1667.

<sup>2</sup> An apparatus for this purpose has been described by Horn, *Chem. Ind.*, 1887, 1, 297.

<sup>3</sup> *Chem. Zeit.*, 1900, 24, 567; 1901, 25, 264.

<sup>4</sup> *J. Soc. Chem. Ind.*, 1902, 21, 670.

## MATCHES AND FIREWORKS

Sample.	A.	B.	C.	D.	E.	F.	G.	H.	I.
Source . . . . .	Foreign	British	Foreign	British	Unknown	Foreign	Unknown	British	British
Colour . . . . .	Dark	Pale	Pale	Pale	Dark	Rather pale	Medium	Pale	Dark
Lustre . . . . .	Dull	High	High	Very high	Moderate	Dull	Moderate	Very high	High
Smell . . . . .	...	...	...	...	Objectionable	...	...	...	...
Character of jelly . . . . .	Coherent, firm	Strong, clean, and "sweet"	Firm and "sweet"	Coherent, clean, "sweet"	Slimy; offensive smell, rapid decomposition	Very slimy, odour most offensive	Strong and coherent, smell satisfactory	Firm and coherent, but odour not good	Particularly firm, coherent, and inodorous
Odour of solution . . . . .	Inoffensive	Good	Good	Good	Objectionable	Very fetid	Good	Not quite "sweet"	Satisfactory
Quality . . . . .	Medium	Very good	Very good	Good	Very poor	Bad	Medium	Low medium	Good
Water . . . . .	15.12	15.38	15.78	15.35	15.67	14.68	13.03	18.03	16.85
Non-gelatinising components (Stelling's test)	4.24	1.91	2.04	1.63	9.94	8.40	2.54	2.64	1.50
Total mineral matter . . . . .	3.01	1.32	1.40	1.59	7.37	1.43	3.24	2.18	1.75
Behaviour of Ash . . . . .	Infusible	Infusible	Infusible	Infusible	Fused	Infusible	Infusible	Infusible	Infusible
Chlorides . . . . .	Slight	Slight	None	Very slight	Large	Trace	Slight	Trace	Absent
Phosphates . . . . .	Trace	Very slight	Trace	Very slight	Large	Considerable	Moderate	Trace	Absent
Viscosity numbers . . . . . (Water = 100)	183	216	223	167	143	133	133	133	200



lead to more definite conclusions than analyses, but some of the chemical data are very useful. Perhaps the best *single* chemical test, is Stelling's—the determination of non-gelatinising matters by precipitating with alcohol, filtering, evaporating a fractional part of the filtrate, and weighing the dried residue. A high result appears to be a *prima facie* indication that the glue, at all events, is below the best standard of quality (see samples E. and F. in the Table). Hygrometric, immersion, jelly-drying, viscosity, and other tests are described in the paper. The viscosity test and Kissling's jelly-consistency test are favourably reviewed, and the hygrometric test (rate of absorption of moisture from air saturated with aqueous vapour) is stated to give useful indications. Finally, it is remarked that whilst it would be rash to form a judgment on glue from a single test, the evidence afforded by a number of tests may be decisive.

#### IV.—METHODS FOR THE DETERMINATION OF FAT IN GLUE

W. Fahrion<sup>1</sup> recommends the following process:—Ten grams of broken glue are warmed on a gently boiling water-bath with 40 c.c. of 8 per cent. alcoholic sodium hydroxide in a porcelain dish, with constant stirring, until the alcohol is completely driven off. If complete solution does not occur, the residue is taken up with alcohol and again evaporated to dryness. The transformation product of the glutin, as also the sodium salts of the fatty and hydroxy-fatty acids dissolve readily; any residue which is found, consists of inorganic matter, and dissolves on subsequent acidification with hydrochloric acid. The acidified solution is heated for about half an hour almost to boiling, then washed into a separating funnel, and after cooling, well shaken with ether and allowed to stand for a considerable time, best overnight. The acid, aqueous liquid is drawn off, and the ethereal solution which contains the fatty acids and the liquid hydroxy-fatty acids is poured off at the top. The solid hydroxy-acids which remain behind in the funnel are dissolved in warm alcohol, the ethereal and alcoholic solutions combined and evaporated, the residue weighed, ignited, and again weighed, and the difference taken as the fat. The results obtained in this way agree satisfactorily among themselves, but are always too low, for two reasons. Firstly, any glycerin present in the glue fat is not determined with the fat, and secondly, the hydroxy-acids are not quite insoluble in acidified water. The error which results in this way is, however, very small, and the figures are throughout higher than those obtained by Kissling's method. For instance, the quantity found for a brown joiner's glue by Kissling's method was 0.21 per cent., by Fahrion's method, 0.51 per cent., and in an almost white skin-glue, by

<sup>1</sup> *Chem. Zeit.*, 1899, 23, 452.

Kissling's method, 0.13, and by Fahrion's method, 0.40 per cent. of fat.

According to Kissling's method<sup>1</sup> (shaking out the glue solution with petroleum ether after acidification with hydrochloric acid), only that part of the fat which is soluble in petroleum ether, is determined. The fat contained in glue is, however, partly oxidised, and oxidised fats are in some cases insoluble in petroleum ether. An example of this is linseed oil. This oil is completely soluble in petroleum ether and in ether, but practically insoluble in alcohol. If exposed to the air in a thin layer, however, processes of oxidation, etc., set in, and these diminish, firstly the solubility in petroleum ether, and then that in ether. The solubility in alcohol increases at first, on the one hand by reason of the formation of free acids by the partial splitting off of glycerin, and on the other hand because the esters of the hydroxy-acids are probably soluble in alcohol. As the drying process continues, however, the solubility in alcohol also diminishes, and the ultimate product (the "linocyn" of Mulder) is practically insoluble in petroleum ether, ether, and alcohol. It can, however, be completely saponified with excess of alcoholic alkali hydroxide, and the non-volatile acids formed can be separated into three parts. The first consists of un-oxidised fatty acids, and is soluble in petroleum ether, ether, and alcohol; the second, for which Fahrion suggests the name "hydroxy-acids," is insoluble in petroleum ether, but soluble in ether and alcohol, and forms a thick, dark red oil; the third, consisting of the solid hydroxy-acids, is insoluble in petroleum ether and ether, but soluble in alcohol, and forms an amorphous brown powder in the dry state.

The raw materials for the manufacture of glue, namely, skin and bones, already contain oxidised fat. Further, the glue decoction is repeatedly heated in presence of air, and finally the drying of the glue brings it into such intimate contact with the air, that the oxidation of the fat probably proceeds further. Indeed, Fahrion found in a skin-glue only 0.08 per cent. of fatty acids as compared with 0.31 per cent. of oxidised fatty acids.

#### V.—DIFFERENTIATION OF ANIMAL AND VEGETABLE GLUE

F. Evers<sup>2</sup> has published an investigation on the differentiation of animal and vegetable glue. The distinction between animal glue and dextrin glue, or between gum and mixtures of gum or dextrin with animal glue, is based upon the well-known reaction towards Fehling's solution, which is reduced in presence of dextrin on boiling. So-called plant glue (albumin glue, gum), which is prepared from wheat gluten and is used for gumming and cloth dressing, is very similar to

<sup>1</sup> *Chem. Zeit.*, 1896, **20**, 698.

<sup>2</sup> *Ibid.*, 1899, **23**, 333.

animal glue in its physical and chemical properties, particularly to inferior bone-glue. Its aqueous solution gives, like animal glue, a voluminous, gelatinous or cheesy coagulum with tannin solution; with a little aluminium sulphate solution it gives no precipitate, or at the most only a slight separation, but with larger quantities of aluminium sulphate it yields a greater amount of a flocculent or cheesy precipitate, whilst with lead acetate it undergoes no change. In general, vegetable glue swells and dissolves with more difficulty in water than animal glue, and the solution gelatinises less readily on cooling. A trustworthy method for distinguishing between the two cannot, however, be based upon this property. Both animal and vegetable glue give flocculent precipitates with concentrated sodium sulphate, which, however, redissolve on warming. If the solution be boiled for some time and treated with lead acetate, animal glue gives a white or pale grey precipitate, whilst vegetable glue, containing as it does, larger quantities of sulphur, generally gives a black precipitate, less frequently a grey one. An aqueous solution of vegetable glue gives on warming with Millon's reagent a violet-red coloration, like all albuminoid substances; in many cases, however, inferior animal glue behaves in the same way.

A simple and trustworthy method for distinguishing between animal and vegetable glue is the following:—The sample of glue (about 1 g.) is dissolved in water (10 c.c.) by warming, a drop of sodium hydroxide being added if necessary. A few grams of common salt or magnesium sulphate are then added, and the whole shaken. The solution of animal glue remains clear, whilst vegetable glue separates almost completely as a voluminous or gelatinous precipitate. Mixtures of animal and vegetable glue can be readily recognised in this way.

#### VI.—PHYSICAL TESTS

(a) **Viscosity.**—According to the investigations of Fels,<sup>1</sup> the consistency of glue is closely related to the quality or binding power. Neither the quantity of water taken up, nor the examination of the mode of fracture gives trustworthy indications of the practical value of a glue, but the viscosity of the solution is a better index of quality. The reason of this is evident; glues which have been prepared under the influence of lime or acids give rise, under certain conditions, to a less consistent jelly than a properly manufactured product, namely, when the lime or acid has not been sufficiently carefully removed from the glue. The decomposition products which result in presence of lime or acids, especially on boiling or steaming the glue-producing substance, as also those which result when too high a steam pressure has been used, diminish the consistency of the jelly, as does also a badly regulated

<sup>1</sup> *Chem. Zeit.*, 1901, 25, 23.



concentration of the glue solution, or even an incipient organic decomposition of this solution.

All of these influences, which come into consideration in the manufacture, affect the finished product, and if the degree of consistency of the jelly obtained from a glue be examined, a true measure for adjudging the quality is obtained. The method is very simply carried out as follows:—

1. *Determination of Moisture.* The sample is broken up, 1 to 2 g. of powdered glue obtained from the fragments, with the help of a file, rasp, or knife, and this quantity is dried for two hours at 100°.

2. *Preparation of the Test Jelly.* About 100 g. of the glue under examination (viz., the broken pieces from which the fine powder was filed) are placed in a beaker of 500 c.c. capacity, and about 400 c.c. of cold water are added; after twenty-four hours the swollen glue is dissolved by heating on a water-bath. The dilution is carried out in such a way that a 15 per cent. jelly results, calculated on the anhydrous glue.

3. *Determination of the Viscosity.* Engler's viscosimeter is especially good for this purpose. First, the viscosity of water at 30° is determined, and used as a unit for the subsequent glue tests. The same determination is then carried out with the 15 per cent. solution of glue, also at 30°. The time of flow of the latter divided by that of water gives a number which expresses the consistency of the glue.

The degrees of viscosity found in this way agree exactly with the behaviour of the glues under water.

Some results obtained by this method of examination are given in the following table. Sample No. 2 was quite slimy after a few hours and sank together to a lump, whereas No. 5 preserved its original form and gave up no particles of jelly, even when scraped with the finger. Further, it was found that Nos. 3 and 5 became a solid jelly after twelve hours, whereas No. 2 was still a thin jelly, and underwent no alteration even after a further period of twenty-four hours:—

Description of Sample.	Substance used, in grams.	Moisture content per cent.	Corresponding quantity of anhydrous substance.	Dissolved to c.c.	Time of outflow of 500 c.c. in seconds.	Viscosity.
1. Light yellow, transparent thick slabs .	95.0	16.3	79.6	530	Time of outflow of water at 30° 90 seconds.	1.65
2. Brown glues, transparent	95.0	14.0	81.7	544		1.36
3. Wine yellow, transparent slabs . .	88.7	15.4	75.1	500		1.91
4. Light yellow slabs, breaking into small pieces . . .	100.0	18.2	81.8	545		1.60
5. Semi-opaque glue .	100.0	15.2	84.8	565		2.21

(b) **Melting Point of the Glue Jelly.**—Kissling is of the opinion<sup>1</sup> that such chemical methods as the determination of the gelatinising matter by precipitation with tannin, or estimations of the percentage of nitrogen, are unsuitable technical methods for adjudging the value of a glue. In a paper by this author<sup>2</sup> on the testing of plates of glue, a method for the determination of the melting point of the glue jelly, and a convenient apparatus for the purpose, are described. The apparatus and method have given good results in the practical manufacture of glue.

A bath of copper or white metal, partially filled with water at 50°, serves as the source of heat. The bath should be filled to a mark placed at two-thirds of its height, and the temperature is kept constant during the experiment. The bath is fitted with a removable cover consisting of a vessel, the bottom of which is covered with a sheet of asbestos upon which rests a ring-shaped receiver. In this a thermometer and the small cylinders containing the glues are placed. The upper vessel is covered with a glass plate. It is advisable to cover the outside of the vessel with asbestos.<sup>3</sup> The method of working is as follows:—Fifteen grams of the glue samples to be tested and 30 g. of distilled water are introduced into small flasks, each fitted with a straight tube about 1 metre long. The flasks are allowed to stand overnight and then heated in boiling water until the glue has dissolved completely, the solution being accelerated by shaking the flasks with a circular motion. The flasks containing the lukewarm glue solutions are then fitted into the glass cylinders, which are made exactly to a specified size and are provided with ring-shaped marks; the cylinders are closed with corks and placed in a holder, the base of which consists of a brass sieve, over which two intermediate discs are fixed, each containing seven holes. The cylinder containing the thermometer is placed in the middle, and contains a concentrated solution (1:1) of the best hide-glue. The receiver thus filled, is allowed to stand for an hour in water, the temperature of which is kept at 15°. After the thermometer vessel and test cylinders have been thus brought to the same temperature, they are quickly brought into the thermostat, which has been fitted up as above, and the melting point of the glue jelly determined. The melting point is the temperature at which the horizontal surface of the jelly begins to become uneven. The higher the melting point, the higher is the content of gelatinising substance. In addition, this simple method gives direct indications as to the degree of firmness of the glue jelly, which is of importance in certain cases, as, for instance, in glueing casks.

As regards the testing of plates of glue, the question whether a glue

<sup>1</sup> *Z. angew. Chem.*, 1903, **16**, 398.

<sup>2</sup> *Chem. Zeit.*, 1900, **24**, 567; 1901, **25**, 264.

<sup>3</sup> This apparatus is supplied by J. Schober, Berlin.

is good or bad, useful or useless, cannot be answered in a general way unless it is so inferior in quality that it can be discarded at once as worthless. In the great majority of instances, the purpose for which it is to be used must be known; hence, a glue can only be designated as unsuitable for a specific purpose.

So far as the binding properties are concerned, numerous experiments have shown that even inferior bone-glues are satisfactory, and hide-glue of high quality scarcely shows any superiority in this respect. If, therefore, only the binding properties have to be taken into consideration, there is no object in using the more expensive hide-glues. This does not hold good for the degree of firmness. Experiment has shown that hide-glues are in general superior to bone-glues in this respect, although some samples of the latter yield moderately firm jellies. As is well known, the method of manufacture plays an important part in reference to this property; the larger the quantity of glutin that is converted to glucose during the manufacture, the less firmness does the jelly possess, and in this respect the manufacture of bone-glue has undergone great improvements.

Considerable weight is attached by some writers to the "Foam-test."<sup>1</sup> Foam is due to over-boiling, which causes peptonisation. A good glue, it is stated, should yield a minimum foam, when the solution is shaken, coupled with a maximum jelly consistency.

(c) **The Binding Power.**—1. *Setterberg's*<sup>2</sup> *Method*. This author soaks strips of unglued paper in a glue solution of known concentration, removes the excess of glue, by pressing between blotting paper, and when dry, estimates the binding power of the glue, by subjecting the strips to tearing tests in a paper-testing machine.

2. *Weidenbusch's test for Binding Power*.<sup>3</sup> This test gives reliable results. Exactly equal prismatic rods of gypsum, 9.2 cm. long, with the side of the transverse section 4 mm., and having a weight of 1.7 g., are dipped in a glue solution for five minutes, then taken out, and allowed to dry. They are then placed on an iron ring, which is fastened in a horizontal position, so as to form the diameter; a dish is hung to the centre of the rod, into which weights are placed until the rod breaks. The better the glue, the greater the weight required to break the rod. By experiment it has been found that the relative adhesive power of skin-glue to that of bone-glue, is as 1.5 : 1; and, further, that glue made from calves' head is better than any other class of glue. The following table bears out these facts:—

<sup>1</sup> Cf. S. R. Trotman and J. E. Hackford, "Conditions affecting the Foaming and Consistency of Glues," *J. Soc. Chem. Ind.*, 1906, 25, 1905.

<sup>2</sup> Post, *Chem. techn. Anal.*, vol. ii., p. 857.

<sup>3</sup> Cf. Hanausek, *Lueger's Lexicon der ges. Technik*, vol. vi., p. 136.



Class of Glue.	Breaking Strain.	Appearance of Fracture.
	Grams.	
Glue from crushed bones, Saybusch . . . . .	291·5	Even, four-sided.
Russian glue from Bohemia . . . . .	304·4	Even, fine-grained.
Saybusch glue, Lyon class . . . . .	351·2	Slightly uneven.
Russian glue from A. Michl, Rehberg . . . . .	434·2	Uneven, with sharp projecting edges.
Cologne glue from A. Michl, Rehberg . . . . .	434·2	Do.
Glue from calves' heads, from Saybusch, Lyon class . . . . .	483·7	Do.
Gypsum rod before dipping in glue . . . . .	103·2	Fairly even, fine grained.

## VII.—COMMERCIAL VARIETIES OF GLUE

*Joiners' Glue* is either skin-glue or bone-glue, or a mixture of the two. *Cologne Glue* is the best and purest skin-glue, and is very much in request on account of its high adhesive power. *Gilders' size* is Cologne glue in thin leaves, bleached by chlorine. *Patent Glue* is a pure, dark-brown bone-glue in thick tablets, without net-markings; it swells greatly in water, and serves for mouldings, buttons, and the like. *Fining Glue* is manufactured from bones in the form of thick, pale-tinted plates, and is used, instead of isinglass, for the fining of wine and beer. *Mouth Glue* is a better quality of bone-glue, scented with lemon essence and sweetened with sugar. *Russian Glue* is a dingy white or brownish white variety of Cologne glue, rendered opaque by the addition of white lead, zinc white, permanent white, or chalk. An improvement in adhesiveness is not aimed at by the additions.

*Glazing* and *Parchment size* are valuable kinds of pure skin-glue, resembling gelatin; parchment size is put on the market in jelly form, packed in small jars, usually with an addition of alum. *Flemish Glue*, consists of thin, yellow leaves, shrunk in both directions, and is used for the production of glue colours and as a glazing material. *Paris Glue* and *Hatters' Glue*,<sup>1</sup> are poor, dark brown, opaque, almost always offensively smelling, soft varieties, used in hat-making because of their considerable hygroscopicity.

*Liquid Glue*. Thirty-eight parts of glue are dissolved in 100 parts of acetic acid; the resulting product remains in the fluid state. A preparation made with nitric acid is known as *Steam Glue*, also as *Russian light* and *dark Steam Glue*. *Glycerin Glue* is obtained by dissolving glue in warm glycerin; small additions of glycerin to steeped glue impart elasticity to the jelly, making it caoutchouc-like and suitable for hectograph compositions. *Chrome Glue* is either a mixture of glue with potassium or ammonium bichromate, or of glue with chrome alum. After drying, the former mixtures are insoluble in

<sup>1</sup> Cf. Valenta, E., *Die Klebe- und Verdickungsmittel*, Kassel, 1884, p. 123.

water. They are used for cementing glass, porcelain, and iron, for finishing and waterproofing materials, and for photographic purposes.

## 2. Gum.<sup>1</sup>

Three sorts of gum are used in the manufacture of matches :—Gum-arabic, gum-senegal, and gum-tragacanth.

(a) *Gum-arabic* forms irregular, brilliant, transparent, brittle pieces, of a white to yellow or brown colour, and varying from the size of a lentil to that of a walnut. The pieces are mostly filled with internal cracks, and are also cracked on the surface, which renders them easy to break and to grind. They do not become damp in the air, show a brilliant conchoidal fracture, and give, with cold water, an almost clear, viscous, slimy, slightly opalescent solution, which can to some extent be drawn out into threads, but which is neither tough nor gelatinous. The solution reacts faintly acid and is very adhesive. Gum-arabic breaks up and dissolves easily in the mouth, and has an insipid and slimy taste.

On account of its high price, it is frequently adulterated, mostly with insoluble cherry-gum, dextrin, etc., and is sometimes bleached with sulphurous acid to make it appear of better quality for certain purposes. This renders it unsuitable for the manufacture of matches. Since the conditions of export from the Soudan have become unfavourable, gum-arabic is adulterated with gum-senegal; indeed, according to Liebermann,<sup>2</sup> the latter is often sold as gum-arabic.

(b) *Gum-senegal* forms round fragments which are larger and more transparent than gum-arabic, and have fewer cracks penetrating to their interior. The pieces frequently contain large air-bubbles, formed like tears, their surface is rough and not brilliant, they vary in colour from almost white to reddish yellow, and their fracture is coarsely conchoidal and very brilliant.

According to Liebermann,<sup>3</sup> gum-senegal forms either colourless, pale yellow, or superficially white pieces, resembling etched glass in appearance, which, however, are bright and transparent internally. The pieces are generally long, straight, or coiled, or cylindrical with concentric rings. Roundish fragments of various sizes are, however, also met with, which have the appearance as if a large drop had become incrustated with smaller pieces after solidifying.

If the gum under examination has not been artificially powdered (by pounding), it is sufficient to observe these external properties to distinguish gum-arabic from gum-senegal. Other gums can also be detected, in this case, according to Liebermann, by the deviation of their appearance from the above.

<sup>1</sup> From J. Kellner's *Die Zündwaaren Fabrikation*, 1897.

<sup>2</sup> *Chem. Zeit.*, 1890, 14, 665.

<sup>3</sup> *Loc. cit.*

Gum-senegal is said to be distinguished from gum-arabic, apart from the above method, by its property of gradually becoming moist on exposure to the air, as also by the fact that it gives only a slight turbidity with mercurous nitrate, and is very markedly thickened by borax. According to Liebermann and Kramsky,<sup>1</sup> however, the assertion that gum-senegal is more hygroscopic than gum-arabic is incorrect. The percentage of water in each kind of gum was determined at 105°, and the dried substance allowed to stand for twenty-four hours in moist air and again weighed. Gum-arabic proved to be slightly the more hygroscopic of the two, as shown by the following data:—

	Gum-senegal.	Gum-arabic.
Water . . . . .	13.39 g.	14.56 g.
Water absorbed in twenty-four hours by the dried samples . . . . .	6.15 g.	6.34 g.

Gum-senegal is more difficultly soluble in water than gum-arabic, and its solution is more slimy and gelatinous and coagulates with a number of chemical reagents, for which reason match heads prepared with this gum are often not very cohesive.

(c) *Gum-tragacanth* comes into commerce in many different varieties. It is tasteless and inodorous, transparent, horny, and tough, so that it is difficult to powder. Only a small part actually dissolves in water; for the most part, it swells up, forming a mucilage, which is not sticky, but nevertheless is highly adhesive, and can be mixed with water if in sufficient quantity. It is, therefore, added to the igniting composition for matches (especially safety matches) in small quantities, firstly, in order to keep the heavier particles in suspension, and secondly, to impart greater hardness to the glue or gum-mass after drying, and thus to protect it from climatic influences.

It is advisable to dry the tragacanth very thoroughly, as this renders it more brittle, and facilitates the grinding. It should be coarsely ground, because it then dissolves more readily, or rather, swells more uniformly and quickly, and is, therefore, more efficacious.

Powdered tragacanth gives a turbid mucilage with 50 parts of water, and this is coloured yellow by sodium hydroxide, when the mixture is heated for a short time on a water-bath. At ordinary temperatures, both powdered tragacanth and the mucilage prepared from it remain completely colourless for hours, on addition of sodium hydroxide. (Reuter.<sup>2</sup>)

A cheap substitute for tragacanth, discovered by Boschau, is a mixture of 20 parts of starch, 6 parts of glue, and 2 parts of glycerin, boiled in water, which is stated to be quite as efficient as tragacanth in its action.

<sup>1</sup> *Chem. Zeit.*, 1890, 14, 665.

<sup>2</sup> *Apoth. Zeit.*, 1890, p. 628.



### 3. Starch.

(The methods of examination are given in Vol. III.)

### 4. Dextrin.

Dextrin is obtained by the treatment of starch with dilute acids, or by prolonged heating to from  $200^{\circ}$  to  $210^{\circ}$ . It forms a white, yellow, or brown powder, according to the method of preparation and the temperature employed, and should be completely soluble in water. The presence of any maltose, which is recognisable by its sweet taste, renders the dextrin useless for the manufacture of matches, since maltose makes the match heads hygroscopic and ultimately incapable of ignition. White dextrin is almost useless for this purpose, the most suitable apparently being of a light brown colour. Dextrin should not be hygroscopic, it should be inodorous, insipid in taste, and should form a mobile powder which is easily soluble in water.

The aqueous solution should be colourless, completely clear, and neither acid nor alkaline. It should give no blue or violet colour with iodine solution, no turbidity with lime water, and no precipitate with tannic acid and baryta water (soluble starch), or with lead acetate. When heated on platinum foil, it should burn without any residue. A blue or violet coloration with iodine indicates unaltered starch or soluble starch. The presence of lime is detected by the addition of ammonium oxalate, oxalic acid by lime water, gum-arabic or mucilage by lead acetate.

Hanofsky<sup>1</sup> recommends the following procedure for testing commercial dextrin:—

1. *Determination of the Constituents Soluble in Cold Water.* Twenty-five grams of the substance are shaken with cold water in a flask of 500 c.c. capacity, filled to the mark, allowed to settle, filtered through a folded filter, and the solution used for the determination of maltose, dextrin, and acidity. The maltose is best determined gravimetrically by Fehling's solution, the solution being boiled for five minutes. The solution is diluted to a quarter of its original strength (10 c.c. Fehling's solution and 40 c.c. water). A preliminary determination is made, to determine how much of the solution is necessary to reduce 10 c.c. of Fehling's solution, and in the second determination, 1 to 2 c.c. less than this quantity are taken and diluted until the whole volume is 57 to 58 c.c.; 113 parts of copper correspond to 100 parts of anhydrous maltose; hence, when the solution is diluted to one-fourth, 113 parts of copper correspond to 91.3 parts maltose, or 1 part of copper corresponds to

<sup>1</sup> *Mitt. des K.K. technol. Gewerbemuseums in Wien*, 1889; *Chem. Zeit. Rep.*, 1889, 13, 148.

0.808 parts of maltose, from which the content of maltose,  $M$ , per 100 g. of the original substance is calculated. For the determination of the dextrin, 50 c.c. of the solution (or 100 c.c. if the quantity of insoluble matter is large) are diluted to 200 c.c. and boiled gently under a reflux condenser with 15 c.c. of hydrochloric acid of sp. gr. 1.125 for two hours. The liquid is then neutralised in a flask of 300 or 500 c.c. capacity, diluted to the mark, and the dextrose determined with Fehling's solution. If the quantity of dextrose found in 100 g. of substance is  $D$ , the quantity of dextrin present in the original substance is  $0.9(D - 1.05 M)$ , since 20 parts of dextrose correspond to 19 parts of maltose. The acidity is determined by titrating 50 c.c. of the solution with  $N/10$  potassium hydroxide, using phenolphthalein as indicator. A certain error is introduced if the volume of the residue in the flask is neglected, but in most cases it is unnecessary to take this into account. If, however, the quantity of insoluble matter is very great, a correction should be applied. If the specific gravity of the residual starch be assumed to be 1.6, the volume of liquid to be deducted from 500 c.c. is,  $V = \frac{p}{1.6}$ , where  $p$  is the quantity of starch in 25 g. of substance. If the quantity of starch is 40 per cent., this volume is only 6.2 c.c.

2. *Determination of the Insoluble Matter.* This consists almost exclusively of starch. Two and a half to three grams of substance are boiled gently for two hours with 200 c.c. of water and 15 c.c. of hydrochloric acid of sp. gr. 1.125, whereby starch, dextrin, and maltose are converted into dextrose. The dextrose is determined with Fehling's solution after neutralising and diluting to 300 or 500 c.c. If the quantity of dextrose found for 100 g. substance is  $D_1$ , the percentage of starch is calculated as  $0.9(D_1 - D)$ .

If the moisture, determined by drying at  $110^\circ$ , is  $W$  per cent., and the ash  $A$  per cent., the quantity of "other organic compounds" is:—

$$100 - (\text{maltose} + \text{dextrin} + \text{starch} + W + A).$$

W. Jettel obtained the following results in several dextrans by this method:—

	Maltose.	Dextrin.	Starch.	Water.	Ash.	Other Organic compounds.	Acidity. c.c. $N/10$ potassium hydroxide.
I.	4.25	47.78	35.55	10.11	0.27	2.04	40.0
II.	10.90	36.75	43.20	7.02	0.39	1.74	26.6
III.	3.75	29.46	58.00	6.85	0.60	1.34	25.3

TESTING AND DIFFERENTIATION OF GUM-ARABIC, GUM-SENEGAL,  
AND DEXTRIN

Liebermann<sup>1</sup> gives the following procedure for this purpose :—

1. External examination of gum-arabic which has not been artificially powdered.
2. External examination of gum-senegal.
3. Both forms of gum are completely soluble in water ; only particles of wood remain behind, which are generally reddish in the case of gum-arabic, and blackish in the case of gum-senegal. These particles of wood are found even in very pure specimens of gum. Other varieties of gum, as, for instance, that of the cherry tree, dissolve only partially in water. A swollen mass remains behind, which dissolves only on prolonged boiling or very long digestion.
4. The aqueous solutions of both sorts of gum give a bluish precipitate with potassium hydroxide and a few drops of copper sulphate solution ; but this is much more pronounced in the case of gum-arabic, and collects in large flakes which rise to the surface in the test tube, whereas the precipitate obtained with gum-senegal is less pronounced, and consists of small flocculi, which remain more uniformly distributed throughout the liquid. These precipitates dissolve but slightly on warming, and no reduction occurs even on vigorous boiling.
5. Solutions of dextrin also give bluish precipitates with potassium hydroxide and copper sulphate, which do not dissolve on shaking in the cold, but dissolve completely on heating, giving rise to clear, dark blue liquids. On boiling for some time, complete reduction of the copper oxide occurs.
6. On prolonged heating with dilute potassium hydroxide in a test tube, solutions of gum-arabic and dextrin become amber yellow, whereas solutions of gum-senegal are scarcely coloured, or assume only a faint yellow tint.
7. Mixtures of gum-arabic and gum-senegal behave towards potassium hydroxide and copper sulphate solution in the same way as gum-senegal alone ; on boiling with potassium hydroxide alone, however, they behave like gum-arabic solutions, the liquid becoming amber yellow.
8. Solutions of mixtures consisting of gum-arabic and dextrin behave like gum-arabic towards potassium hydroxide and copper sulphate, as regards the appearance of the precipitate. On boiling for some time, however, reduction takes place, if the quantity of dextrin is not too small. The same applies to mixtures of gum-senegal and dextrin.
9. If the quantity of dextrin be too small, the reduction may not take place. In such cases, the precipitate obtained with potassium hydroxide and copper sulphate must be filtered off, after moderate

<sup>1</sup> *Chem. Zeit.*, 1890, 14, 665.



warming. The filtrate, which contains no gum, but is still somewhat milky and turbid, is boiled. A distinct separation of red cuprous oxide (or yellow hydroxide) shows the presence of dextrin.

10. The separation must be carried out in the same way when mixtures of both sorts of gum with dextrin are under investigation. The copper precipitate, containing the acid gum products, is washed with distilled water, dissolved in hydrochloric acid, and this solution precipitated with excess of alcohol. The precipitate is allowed to subside for one and a half to two days, the liquid then decanted, and the transparent disc of gum, which remains at the bottom of the vessel, washed with alcohol. The small quantity of alcohol remaining behind is allowed to evaporate; or, the gum is dissolved directly in hot water and the aqueous solution tested for gum-arabic or gum-senegal, as indicated in Nos. 4, 6, and 7.

*The Examination of Gum-arabic* can also be carried out as follows:—

A. Appearance of the gum, according to 1 and 2, if the gum has not been pulverised.

B. Solution of the powdered substance in luke-warm water. Observations as in No. 3. If the substance dissolves only partially, leaving a swollen gelatinous mass, it consists of cherry gum or a similar gum ("gummi nostras"), or of a mixture containing such gums. If the substance dissolves, all but a turbidity and a few particles of wood, proceed to:—

C. The aqueous solution is treated with excess of potassium hydroxide and some copper sulphate, gently warmed, and filtered:—

(a) *The Filtrate*, which may contain dextrin, is tested according to No. 9.

(b) *The Precipitate* is examined as in No. 10. If the aqueous solution of gum acids, prepared as described in No. 10, be treated with an excess of potassium hydroxide and some copper sulphate added, a precipitate results, which either agglomerates and rises to the surface, or remains in the form of small flakes uniformly suspended throughout the liquid.

*Precipitate Agglomerates.*

Gum-arabic.

(The aqueous solution becomes amber yellow on treatment with potassium hydroxide.)

*Precipitate does not Agglomerate.*

Gum-senegal, or a mixture of gum-senegal and gum-arabic.

(The aqueous solution is boiled with potassium hydroxide.)

*Amber Yellow  
Colour.*

—  
Mixture of gum-  
arabic and  
gum-senegal.

*No Colour, or Pale  
Yellow.*

—  
Gum-senegal.

*Detection of Gum-substitutes.*<sup>1</sup> Of late years, good, strongly adhesive gums have come on the market only in small quantities and at high prices. As a consequence, substitutes have been sought for, and have been exported in large quantities from South America, Australia, etc. Some of these have served the purposes of gum satisfactorily for some technical uses; they proved to be easily soluble, but were all inferior to genuine gum-arabic in adhesiveness. Some kinds, however, although of inviting appearance, proved to be quite insoluble, only swelling up when placed in hot water. It has been pointed out<sup>2</sup> that such gums could be rendered soluble by boiling under high pressure. This is probably correct, but gum so dissolved possesses a very inferior adhesive power, not even equal to that of starch paste; it could, therefore, be only used for thickening purposes; even in this case starch or tragacanth is greatly preferable.

As long as such gum-substitutes came in the unmixed state into the market, they were easily recognised. Recently, however, such products have been ground to a coarse powder, and mixed with an equal part of genuine gum-gheziri and sold as granulated gum. A simple solution test does not show the presence of substitutes, since the swollen gelatinous particles of the substitute remain suspended, and are completely invisible. In order to detect such adulteration with certainty, the following simple method may be recommended.

The suspected gum is covered with ten times its quantity of hot water, and allowed to stand for three or four hours, with frequent stirring. When the insoluble matter has subsided, half the liquid is poured off, replaced by the same quantity of cold water, and again well stirred. This process is repeated twice within an hour. The last mixture separates after short standing into two parts, the upper layer consisting of water, and the lower layer of a gelatinous, highly refractive mass. In this way, the presence of even 5 per cent. of adulteration can be detected with certainty.

#### E. COLOURING MATTERS

Red lead, manganese peroxide, ochre, umber, smalt, ultramarine, and various coal tar dyes are employed.

#### IV.—MATERIALS FOR THE STRIKING SURFACE

These are the same as for the match compositions. Manganese peroxide, the sulphides of antimony, powdered charcoal, amorphous phosphorus, potassium chlorate, glass powder, etc., as frictional

<sup>1</sup> Cf. A. Jaksch, *Chem. Zeit.*, 1891, 15, 77.

<sup>2</sup> *Chem. Zeit.*, 1887, 11, 1566; *Chem. Zeit. Rep.*, 1888, 12, 203.

materials; chalk, etc., as filling materials; umber and the like as colouring matters; glue, gelatin, and dextrin as binding materials. (See III., A to E, pp. 528 *et seq.*)

#### V.—MATCH COMPOSITIONS<sup>1</sup>

##### A. COMPOSITIONS FOR MATCHES WHICH STRIKE ON ANY SURFACE<sup>2</sup>

This class includes not only the matches which in some countries are still made with ordinary phosphorus, but also matches free from phosphorus, and those which contain red phosphorus, or a phosphorus and sulphur compound. For a great number of years attempts have been made to eliminate the use of phosphorus, also of especial striking surfaces. Many of the proposed substitutes for phosphorus, however, have been too expensive, some too little inflammable, some too unstable, and some only available for paraffined matches.

In those match compositions which contain no white phosphorus, sulphur is mixed with such substances as amorphous phosphorus, phosphorus sesquisulphide, antimony sulphide, thiocyanates, and cyanides of metals, etc.; or easily inflammable substances, like charcoal, the salts of fatty acids (stearates), carbon compounds, such as naphthalene and phenanthrene, as well as shellac and resins. As oxidising agents, besides those already mentioned, such as potassium permanganate and nitro-compounds, guncotton, aromatic nitro-compounds, such as trinitrophenol (picric acid) and picrates, have been tried. These last substances are explosives; their properties are described in this Vol., p. 508. So as to retard the combustion and to ensure a complete ignition of the composition, a small quantity of a complex metallic cyanide, such as Prussian blue, Turnbull's blue, or even the material used in gas purification, is added; this contains free sulphur, thiocyanates, and complex metallic cyanides.

Rossel gives the following two recipes for the preparation of match compositions:—(1) 10 parts of potassium chlorate, 7 parts of pure and freshly precipitated lead thiosulphate, 2.5 to 2.9 parts of antimony trisulphide, 0.25 parts of gelatine. (2) 300 parts of powdered glass, 120 parts of manganese peroxide, 160 parts of potassium bichromate, and 90 parts of flowers of sulphur; these are mixed together in water and finely ground. In another case, 300 parts of gum-arabic and 210 parts of glue are dissolved in water, and 1800 parts of well-powdered and sieved potassium chlorate are added; the following substances are then added consecutively, each being finely powdered:—600 parts of lead thiosulphate, 450 parts of red lead, and 25 parts of barium thio-

<sup>1</sup> For further details, *cf.* Muspratt, *Handbuch der technischen Chemie*, 1907, **10**, pp. 707 *et seq.*

<sup>2</sup> *Cf.* E. G. Clayton, "Matches," *Dict. Appl. Chem.*, 1911, vol. ii.



sulphate. Rossel gives particulars also of the following composition, containing red phosphorus:—450 parts of potassium chlorate, 100 parts of potassium bichromate, 75 parts of powdered glass, and 60 parts of sulphur (washed flowers of sulphur or powdered roll-sulphur), 25 parts of *caput mortuum* (iron oxide), 7 to 8 parts of red amorphous phosphorus, 110 parts of gum-arabic, and 30 parts of gum-tragacanth.

Craveri<sup>1</sup> has proposed the use of persulphocyanic acid, which is supposed not to react when hammered or rubbed, is claimed to be non-poisonous, from every point of view to be quite harmless during the manufacture of the match compositions, and to be cheaper than phosphorus.

The composition made by Bohy, Gallay, & Co., of Nyon,<sup>2</sup> contains salts of hypophosphorous acid, mainly the calcium salt, in place of ordinary or amorphous phosphorus. Calcium, barium, and strontium hypophosphite only ignite at a high temperature; if, however, they are mixed with potassium chlorate or nitrate, or any other oxidising agent, ignition takes place very readily. This composition is made as follows:—210 g. of glue and 30 g. of gum-tragacanth are allowed to soften for twelve hours in water, then warmed and boiled; 25 g. of turpentine are added, then 1 kg. of potassium chlorate, 200 g. of sulphur, 150 to 200 g. of a hypophosphite (calcium, barium, or strontium salt), 5 to 10 g. of potassium bichromate, 125 to 150 g. of barium chromate, 200 to 250 g. of powdered glass, and 10 g. of colouring matter. Another composition can be obtained by the further addition of 150 g. of naphthol yellow, or in place of this, 100 g. of picric acid.

For the so-called "Imperial" composition, used in Germany (Schwiening's composition),<sup>3</sup> see p. 534.

Older formulæ show that early attempts were made to use compounds of phosphorus and sulphur, but that owing to their too easy inflammability, the use of the liquid sulphides, or supposed sulphides of phosphorus, was considerably restricted. Even before Sévène and Cahen (p. 531), Bals<sup>4</sup> had recommended fusing together sulphur and red phosphorus, but the result was not equivalent to phosphorus sesquisulphide. The Sévène-Cahen process was taken up by the French Government, and it is said that the French public did not notice any difference, on the introduction of the so-called "S. and C." matches, containing this substitute for phosphorus.

The "S. and C." composition varies, according to whether it is to be used for paraffined or sulphured splints, or for waxed threads. The ordinary composition is as follows:—6 parts of phosphorus sesquisulphide, 24 parts of potassium chlorate, 6 parts of zinc oxide (zinc

<sup>1</sup> Eng. Pats. 18563 and 27520, 1897.

<sup>2</sup> Eng. Pat. 16037, 1898; Ger. Pat. 106734 f.

<sup>3</sup> Ger. Pat. 86203.

<sup>4</sup> Ger. Pat. 89700.

white), 6 parts of red ochre, 6 parts of powdered glass, 6 parts of glue, and 34 parts of water. It is easy, by manipulation, to make these matches either more or less inflammable. The mechanical processes are much the same in this case as in the case of phosphorus matches.

For some years past, "strike-anywhere" matches have been successfully manufactured in Great Britain, on a very large scale, with phosphorus sesquisulphide compositions.

The Chemische Fabrik Griesheim-Elektron has placed on the market a product,<sup>1</sup> called "Sulfophosphit," which consists of zinc, phosphorus, and sulphur. It is stated that both paraffined and sulphured matches can be made with this substance, with any required degree of inflammability. "Sulfophosphit" is claimed to be more stable, under atmospheric influences, than red phosphorus and phosphorus sesquisulphide; the cost also is alleged to be low.<sup>2</sup>

The basis of another dipping composition, made by R. Gans,<sup>3</sup> is a mixture of "sulfocuprobariumpolythionate" and potassium chlorate. The composition is said to be comparatively insensible to warmth, and to keep for a long time. The splints, after dipping, are coated with a spirit or water varnish. This new composition is said to be more inflammable than that of Schwiening.

#### B. COMPOSITIONS FOR SAFETY MATCHES WHICH REQUIRE A SPECIAL STRIKING SURFACE (SWEDISH MATCHES)

*Brown Safety Match Composition* (Kellner). One hundred and fifty parts of gum-senegal are dissolved in 200 parts of water, and at the same time 20 parts of powdered tragacanth are digested in 300 parts of water for twenty-four hours; these solutions are united and boiled, and 100 parts of powdered and sifted potassium chlorate introduced. To this is added a finely powdered and thoroughly mixed mixture of 125 parts of potassium bichromate, 30 parts of sulphur (crushed roll-sulphur or washed flowers of sulphur), 33 parts of antimony trisulphide, 50 parts of powdered colophony, 200 parts of minium or of lead peroxide, 100 parts of umber or terra di Sienna, 100 parts of powdered glass or powdered pumice stone, and lastly 150 parts of hot water.

*Composition for the Striking Surface.* Four hundred parts of dextrin are mixed with 400 parts of water, boiled, and allowed to cool; with this is mixed a thin paste of red phosphorus, which has been made by stirring 1000 parts of red phosphorus with 2000 parts of water, allowing to stand, and pouring off the excess of water. Then, 200 parts of prepared chalk (the mass swells up, owing to evolution of carbon dioxide), 300 parts of umber, and 1000 parts of finest powdered antimony sulphide are added, and the whole mixture passed through a mill.

<sup>1</sup> Ger. Pat. 153188, 1902.

<sup>2</sup> Cf. *Allgem. chem. Zeit.*, 1906, p. 207.

<sup>3</sup> Ger. Pat. 157424, 1903.

On account of the prohibition of the use of phosphorus in Switzerland, Rossel prepared the following composition:—Ten parts of gum-arabic, 300 parts of gum-tragacanth, 53.8 parts of potassium chlorate, 6 parts of *caput mortuum*, 12 parts of powdered glass, 5 parts of potassium bichromate, 3 parts of sulphur, 1.2 parts of chalk or colophony, and 6 parts of manganese peroxide. The striking surface for this composition consisted of 5 parts of antimony sulphide, 3 parts of amorphous phosphorus,  $1\frac{1}{2}$  parts of manganese peroxide, and 4 parts of glue.<sup>1</sup>

A phosphorus-free striking surface, recommended by Craveri,<sup>2</sup> on which any safety match will ignite, is made up as follows:—Two parts of a thiocyanate compound, 1 part of persulphocyanic acid, 0.5 parts of potassium xanthate, 4 parts of antimony sulphide, and, as a binding material, 1 part of gelatin.

## VI.—THE CHEMICAL EXAMINATION OF MATCH COMPOSITIONS

The composition, when examined under the magnifying glass, should be as uniform as possible, and it is important that no particles of phosphorus should be visible.

The following method of examination is recommended by Bolley,<sup>3</sup> for the purpose of determining the constituents of a match composition. The matches are placed in water at a maximum temperature of 20°, in a porcelain basin, the swollen heads removed by mechanical means, and after having been broken up under the water, digested and continually stirred (in the absence of phosphorus, the mixture can be boiled), and then separated by filtration.

1. The filtrate, which may contain potassium chlorate, potassium nitrate, lead nitrate, potassium chromate, potassium ferrocyanide, gum, glue, and dextrin, as well as other substances that are soluble in water, is divided into several portions. One of these is tested for lead, another for chlorate. Another portion is evaporated and ignited; if the residue, on moistening, gives an alkaline reaction, a nitrate is present. Ferrocyanic acid is tested for with a ferric salt. To determine the presence of gum or glue, a rather larger portion of the same filtrate is evaporated to dryness with sodium hydroxide; on heating a portion of this residue in a tube, the presence of glue or albuminous matter is indicated by the evolution of ammonia gas, which can be tested for in the usual manner, either by smell, or with hydrochloric acid, or with turmeric paper. Gum and glue are precipitated from the solution, on the addition of alcohol. The presence of dextrin in the solution is determined by the addition of a few drops of a solution of iodine, when a pale reddish blue coloration is formed.

<sup>1</sup> Jacobsen, *Chem. techn. Repertorium*, 1881, 1, 150.

<sup>2</sup> Ger. Pat. 114279.

<sup>3</sup> Cf. Muspratt's *Handbuch der technischen Chemie*, vol. x.



2. The residue on the filter paper is digested with alcohol, so as to extract stearic acid, paraffin and resins. To extract wax, it is necessary to boil with the alcohol; this is not permissible, however, in the presence of phosphorus. The alcoholic filtrate, after evaporation, yields a substance, from the consistency, fusibility, etc. (solubility in ether, fractional crystallisation, and melting point), of which, conclusions can be drawn as to the nature of the residue. If phosphorus be present in the residue, it can be removed before the digestion with alcohol, by treatment with nitric acid, when it is converted into phosphoric acid, which is recognisable by the usual means.

Matches containing phosphorus become luminescent in the dark, and when moistened with water give the characteristic smell of phosphorus.

3. The original residue, which remains after the digestion with water, will evolve chlorine on heating with hydrochloric acid, if lead peroxide, red lead, or manganese peroxide be present; the smell of sulphurous acid denotes sulphites, and lead, manganese, iron, and antimony can be tested for in the residual solution. The presence of lead peroxide, or of red lead, is recognised from the colour of the match head. Ochre remains partly, and smalt completely, undissolved; both can be recognised with the blowpipe, whereas ultramarine is decomposed by hydrochloric acid, evolving sulphuretted hydrogen. Charcoal, sand, and powdered glass remain undissolved in hydrochloric acid, and can be identified with a magnifying glass; sulphur can be recognised by its colour, by the smell on burning, or it can be extracted with carbon bisulphide.

In the older literature, very little is to be found upon the subject of the examination of matches, especially as regards tests for inflammability, hygroscopicity, etc. Their behaviour when in use was regarded as sufficient. Even in more recent literature, there is not much information on these matters. But in consequence of the prohibition of the use of white phosphorus in various countries, new match compositions are now coming forward, and their chemical and physical examination will become necessary.

There are but few published accounts of recent work; mention may be made of that of Wiederhold,<sup>1</sup> H. Schwarze,<sup>2</sup> and B. Schulze; that of the last deals with the inflammability, after-glow, etc., as well as with the utility of different kinds of matches.<sup>3</sup> T. Schlösing has done some work on the gases given off on the combustion of compositions containing red phosphorus, and sulphur compounds of antimony and lead. The most recent work is that of K. Fischer.<sup>4</sup>

<sup>1</sup> *Dingl. polyt. J.*, 1861, 161, 221, 268; 1862, 163, 203, 296.

<sup>2</sup> *Ibid.*, 1876, 219, 243.

<sup>3</sup> *Ibid.*, 1892, 283, 274.

<sup>4</sup> *Arbeiten aus den Kaiserlichen Gesundheitsamt.*, 19, 305.

## A. EXAMINATION FOR PHOSPHORUS

The recognition of phosphorus is very much simplified by its power of luminescence in the dark; but in the case of a small quantity of phosphorus in a very large quantity of matter, for instance, in poisoning cases, either in a quantity of food, or in the stomach contents, this luminescence does not show, even when friction is applied. The material is firstly examined for an odour of phosphoretted hydrogen, or for ozone, which would denote the presence of free phosphorus. Strips of paper, soaked respectively in a silver salt solution and in an alkaline lead solution, are hung up over the material for examination. If phosphorus be present, the silver paper only will be blackened; should both papers turn black, the presence of sulphuretted hydrogen is proved, but not the presence of phosphorus; that is to say, this test for phosphorus fails in the presence of sulphuretted hydrogen. Attempts can also be made, by treating the matter with water, to collect any minute floating particles of phosphorus in a filter, and if this be successful, they can be oxidised by nitric acid to phosphoric acid and tested for in the usual way.

The following method, however, due to Mitscherlich, is the safest:—The mass is acidified with sulphuric acid, and distilled with steam, the vapours being passed through a vertical condenser; if phosphorus be present, it is vaporised with the steam, and can be recognised as a luminescent ring, which moves up and down in the condenser. The test is conducted in a darkened room; it is possible by this means to detect 0.00001 parts of phosphorus. It is often possible to find small particles of phosphorus in the distillate, and to obtain the test for phosphorous acid. The phosphorus and phosphorous acid are treated separately with strong chlorine water, and thus oxidised to phosphoric acid, which is estimated in the usual manner with magnesium sulphate, ammonia, and ammonium chloride, as magnesium ammonium phosphate.

Care must be taken in carrying out this test, that alcohol and ether, should they be present, do not prevent the luminescence of the vapours. Turpentine and other volatile oils, as well as phenol and creosote, often completely prevent it; furthermore, red phosphorus does not produce this luminescence, but mixtures of sulphur and phosphorus, such as are found in match heads, will cause it. According to Polstorff and Mensching,<sup>1</sup> the luminescence is also hindered by the presence of mercury salts. Copper salts and sulphuretted hydrogen also are said to interfere. Even after continued distillation, the whole of the phosphorus will not be found in the distillate; O. Schifferdecker calculates that for every milligram of phosphorus in the distillate, the original substance contained 1.5 to 2.0 mg.

<sup>1</sup> *Ber.*, 1886, 19, 1763.

The presence of potassium chlorate in match compositions greatly interferes with the testing for phosphorus, a subject which has been especially examined by K. Fischer.<sup>1</sup> To determine to what extent potassium chlorate prevents Mitscherlich's test, small quantities of ordinary phosphorus were mixed with varying quantities of potassium chlorate, and distilled with dilute sulphuric acid; it was found that the phosphorescence ceased immediately the dilute sulphuric acid commenced to react on the potassium chlorate, liberating chlorine compounds. In such instances a very faint phosphorescence was often visible at the very commencement of the distillation, but this ceased in a very few seconds, so that it could only be seen by making a very careful observation. In one experiment 0.002 g. of phosphorus were distilled with 50 c.c. of water and 10 c.c. of dilute sulphuric acid; a strong luminescence was visible during the whole period, about an hour, of the distillation. If, however, 1 g. of potassium chlorate was added to these same quantities, the phosphorescence was visible for barely five seconds. Phosphoric acid could be detected both in the distillate and also in the residue in the flask. From these, and from many other experiments in which the quantities of phosphorus, sulphuric acid, and potassium chlorate were varied, and which all gave the same result, it is clear that in the presence of potassium chlorate, it is very easy to miss phosphorus by Mitscherlich's test. The non-appearance of luminescence is undoubtedly due to the fact that the chloric acid liberated from the potassium chlorate by the sulphuric acid, oxidises the phosphorus to phosphorous or phosphoric acid, before the phosphorus can volatilise.

To prevent the formation of chloric acid, in testing match compositions for phosphorus by Mitscherlich's method, it is advisable to wash the sample several times with cold water, so as to eliminate the chlorate, before distilling. If substances soluble in water are to be determined, the two tests can be combined. The washing with water, which occupies some time, can be avoided by using tartaric acid for the distillation instead of sulphuric acid; this does not influence the phosphorus test, even in the presence of potassium chlorate.

Another means of detecting phosphorus, described by Dusart<sup>2</sup> and Blondlot,<sup>3</sup> is based on the fact that small quantities of phosphorus, also phosphorous acid and silver phosphide, give with nascent hydrogen, phosphoretted hydrogen, which can be recognised in the hydrogen flame, by the emerald green colour, which it imparts to it; the whole flame becomes green, as soon as a porcelain basin is held in it. The hydrogen must of course be free from sulphuretted hydrogen, and for this purpose is passed through a tube containing pumice-stone soaked in potassium

<sup>1</sup> *Arbeiten aus dem Kaiserlichen Gesundheitsamt*, 19, 307.

<sup>2</sup> *Jahresber. d. Chemie*, 1856, p. 724.    <sup>3</sup> *Ibid.*, 1861, p. 821; *Z. anal. Chem.*, 1861, I, 129.



hydroxide, before lighting, otherwise the flame would appear blue; also the gas exit-tube should have a platinum-covered tip, as the sodium contents of the glass will otherwise colour the flame. The substances containing phosphorus must not be introduced directly into the hydrogen-generating mixture, as they easily prevent the formation of the green flame. But the phosphorous acid or phosphorus particles obtained by Mitscherlich's test, can be introduced into a suitable mixture of zinc and dilute sulphuric acid; or silver phosphide, which is obtained as a black powder by heating the acidified phosphorus-containing matter in a current of carbon dioxide, and passing the gas into a solution of silver nitrate, may be so introduced. The green flame appears in the presence of the smallest trace of phosphorus, and, according to Christoffe and Beilstein, gives a spectrum with three green lines, of which the two strongest are in the green, and the weakest in the yellow. Dusart's test has been modified by Dalmon in such a manner that the whole of the organic matter containing phosphorus is treated with hydrogen. The gas is passed through a long, drawn-out glass tube, bent upwards at right angles, and is lighted at the end; if a narrow glass tube is pushed over the jet, the flame shortens, and appears green, for the whole length of the tube, and when the tube is pushed down further, the flame shortens still more, becomes dark blue, and if the glass tube is slowly drawn away at this moment, a magnificent emerald-green flame-ring appears, passing up the tube with greater or less velocity. The phosphorus-charged hydrogen, generated in this way, luminesces in a dark room, without the gas being ignited.

Other methods for the detection of phosphorus in organic substances have been described by Nicklès<sup>1</sup> and Bastelaer.<sup>2</sup>

With regard to the period during which phosphorus will remain in organic matter and can be tested for, Medicus<sup>3</sup> gives the following data:—Neumann found phosphorus in a corpse after it had been buried for fourteen days. Dragendorff mentions a case, in which he was able to detect phosphorus in the secretions in a corpse that had been buried for several weeks and afterwards exhumed. Fischer and Müller were able to detect phosphorus in the body of a guinea-pig, which had been buried for eight weeks. On the other hand, Herapath was unable to detect a trace of phosphorus twenty-three days after death; Brandes could find no phosphorus in the corpse of a child after three weeks, but could detect its acids. Medicus was able to detect phosphorus for half an hour by Mitscherlich's test twenty-three days after poisoning; the sulphuric acid solution, after filtering, gave a gas containing phosphorus on treatment with zinc and hydrochloric acid.

<sup>1</sup> *Z. anal. Chem.*, 1870, 9, 71.

<sup>2</sup> *N. Jahresber. d. Pharm.*, 40, p. 24.

<sup>3</sup> *Z. anal. Chem.*, 1880, 19, 164.

## B. TESTING FOR ORDINARY PHOSPHORUS IN MATCH HEADS

**Prohibition of the Use of White Phosphorus.**—Subsequent to conferences held at Berne in 1905-6, certain European countries discontinued the use of white phosphorus in the manufacture of matches. In Germany a law relating to the use of phosphorus was passed as early as 1903, and subsequently the law that white phosphorus should cease to be used for the manufacture of matches after 1st January 1907 was approved. The United Kingdom for a while held back, but in 1908 British manufacturers and holders of patent rights in substitutes for phosphorus decided to stop using white phosphorus, provided that the importation of white phosphorus were prohibited. Accordingly the "White Phosphorus Matches Prohibition Act (8 Edward VII., 1908, chapter 42)" was passed on 21st December 1908, and came into force on 1st January 1910.<sup>1</sup> According to this Act:—"It shall not be lawful for any person to use white phosphorus in the manufacture of matches, and any factory in which white phosphorus is so used shall be deemed to be a factory not kept in conformity with the Factory and Workshop Act, 1901. . . . It shall not be lawful for any person to sell or to offer or expose for sale . . . any matches made with white phosphorus. . . . It shall not be lawful to import into the United Kingdom matches made with white phosphorus, and matches so made shall be included among the goods enumerated and described in the table of prohibitions and restrictions contained in section 42 of the Customs Consolidated Act, 1876."

**Detection of White Phosphorus.**—It is now necessary, therefore, to test for white phosphorus in match heads, in cases where its presence is suspected. Hitherto no exact method has been advanced, suitable for the detection of white phosphorus under all conditions.

On the one hand, the examination of phosphorus sesquisulphide, which is frequently present, is, according to Friedheim,<sup>1</sup> difficult, because the sulphur-phosphorus compounds gradually decompose into compounds containing less sulphur, with separation of white phosphorus; and on the other hand, the detection of phosphorus in matches in presence of potassium chlorate cannot be carried out by the ordinary methods of analysis.

In some cases it is possible, when examining match heads stated to contain no white phosphorus, and to which no white phosphorus has been added as such, to demonstrate the presence of this substance, yet it cannot be ascertained whether it was added, or whether it was re-formed from phosphorus sesquisulphide. Again, in other cases, no phosphorus may be detectable, notwithstanding

<sup>1</sup> Cf. *J. Soc. Chem. Ind.*, 1909, 28, 43.

<sup>2</sup> *Fifth International Congress for Applied Chemistry*, Berlin, 1903.

its presence, because the test sometimes fails in presence of potassium chlorate (*cf.* p. 561).

To test for ordinary phosphorus, at least twenty-five match heads are placed directly in a Mitscherlich apparatus, with 50 c.c. of water and 10 c.c. of dilute sulphuric acid. The mixture is heated over a flame, without the introduction of steam (*cf.* p. 560); if potassium chlorate be present, the phosphorescence may not appear (*cf.* p. 561); but on the other hand, phosphorus sulphide is capable of producing a luminescence, which, though different from that caused by phosphorus, may be mistaken for it.<sup>1</sup> In the first case, either the substances soluble in water, including the potassium chlorate, must first be removed from the match heads with cold water, or the test must be carried out with tartaric acid.

To test for ordinary phosphorus in the presence of phosphorus sulphide (phosphorus sesquisulphide,  $P_4S_3$ ), the following process, due to R. Schenck and E. Scharff,<sup>2</sup> can be employed. This method is based on the property of ordinary phosphorus, when oxidised to phosphorus trioxide, of ionising the air, which then becomes capable of conducting electricity. Phosphorus and sulphur compounds, even if they luminesce, do not produce this effect.

The apparatus employed<sup>3</sup> (Fig. 78) consists of two parts, connected by a glass tube, viz., the vessel *a*, for generating the phosphorised air, and the electroscope *b*. The former is a test tube with a side connection, and a ground glass stopper, through which the air delivery tube passes, reaching nearly to the bottom of the test tube. To the side connection is attached a glass tube by means of rubber tubing, which delivers the phosphorised air to the cylindrical condenser *c*, the removable top *d* of which carries the electroscope. Within the outer cylinder *c* is an insulated, cylindrical test electrode suspended from the electroscope.

The phosphorus oxidation products are prevented from entering the inside of the electroscope case *b*, from *c*, by two insulated plates, which can be removed and cleaned, and through which the carrier of the test electrode passes and fits closely. A small piece of sodium is put in *c* to prevent access of moisture. A rod, by means of which the test electrode can be charged, passes through the lid of the cylinder *c*, which is well insulated and has a properly insulated handle.

To charge the electroscope, the rod is pushed down close to the test electrode, and a Zamboni's dry pile brought up to it and then removed; after charging, that is, when the aluminium leaves of the electroscope are apart, the rod is drawn up again.

<sup>1</sup> *Cf.* J. Mai and F. Schaffer, *Ber.*, 1903, 36, 870; also E. G. Clayton, *Proc. Chem. Soc.*, 1902, 18, 129; 1903, 19, 231.

<sup>2</sup> *Ber.*, 1906, 39, 1522.

<sup>3</sup> Made by Rink, of the Physiological Institute of the Marburg University.



To carry out the test, some of the match composition, for instance a few softened and ground match heads, mixed with zinc oxide (to hold back sulphuretted hydrogen), are placed in the test tube *a*, which is surrounded by warm water at  $50^{\circ}$ ; after the electroscope has been charged, air is blown through about ten times successively with the aid of a rubber ball, or the air can be drawn through by means of an aspirator, care being taken to place a bottle of several litres capacity, to catch any solid matter that might get sucked over, between the test-tube *a* and the cylinder *c*.

In the presence of the smallest quantities of ordinary phosphorus, the electroscope will be discharged, that is to say, the aluminium leaves

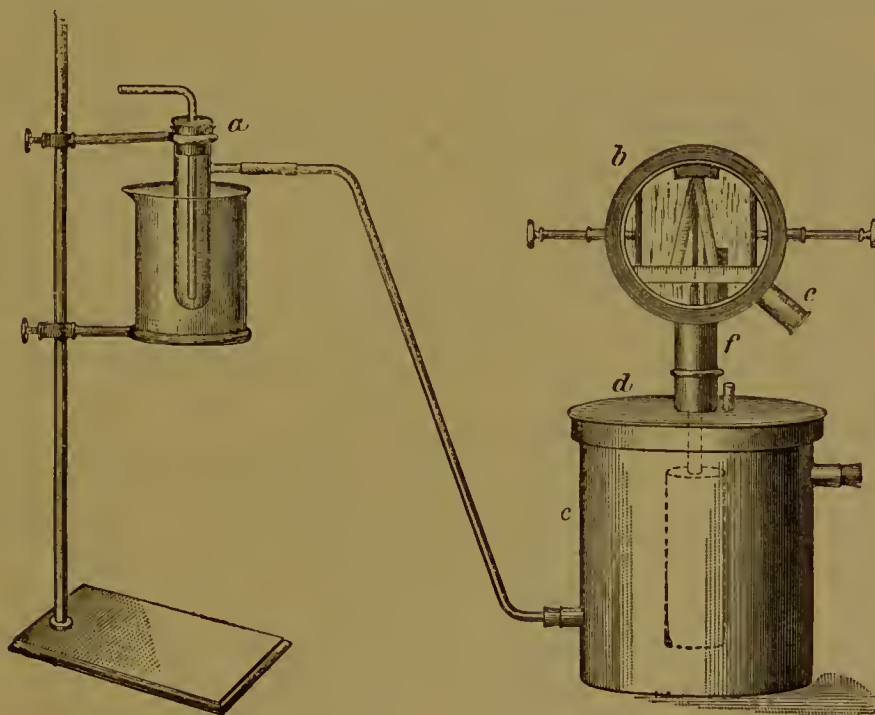


FIG. 78.

fall together suddenly. Under normal conditions this takes place only slowly. The leaves ordinarily move through 0.2 to 0.5 divisions of the scale in five minutes.

The following method for the detection of white phosphorus in matches is based upon that of Aronstein.<sup>1</sup> One hundred or more match heads are moistened with water, and then boiled with carbon bisulphide for two hours under a reflux condenser. The cooled extract is filtered through a dry filter paper into another flask, and the carbon bisulphide distilled off on a water-bath. The flask containing the residue is at once connected with an apparatus by which, firstly, carbon dioxide, and secondly, dry air can be introduced. While the current of carbon dioxide is driving off the small quantity of carbon bisulphide

<sup>1</sup> *J. Chem. Soc. Abstr.*, 1906, p. 705.

remaining in the flask, the temperature of the water in which the flask is immersed is gradually raised from about  $15^{\circ}$  to  $30^{\circ}$ . The room having been previously darkened, dry air is admitted into the flask at different and increasing temperatures, the current of carbonic acid gas meanwhile being almost entirely turned off. Careful watch is kept for any sign of luminescence. If there be none at  $30^{\circ}$ , the temperature is gradually raised. In most cases, when white phosphorus is present, luminescence is seen below  $35^{\circ}$ ; very occasionally it may first appear at as high a temperature as  $55^{\circ}$ . The glow temperatures observed in two recent experiments (December 1910), with matches containing white phosphorus, were  $23^{\circ}$  and  $25^{\circ}$  (E. G. Clayton). The lowest limit of glow for phosphorus sesquisulphide, in the absence of white phosphorus, is generally about  $60^{\circ}$ ,<sup>1</sup> so that this process can be applied to the detection of small quantities of white phosphorus in the presence of considerable amounts of phosphorus sesquisulphide.

According to C. van Eijk,<sup>2</sup> a tube containing phosphorus sesquisulphide is not luminescent below  $70^{\circ}$ , but if 0.02 per cent. of white phosphorus be present a glow appears below  $60^{\circ}$ . An alternative plan is to extract with carbon bisulphide, evaporate off the solvent, and distil the residue with a solution of lead acetate. Sesquisulphide of phosphorus is decomposed, and luminescence appears only in the presence of white phosphorus.

*T. E. Thorpe's Sublimation Test* for white phosphorus is carried out as follows<sup>3</sup>:—A few grams of the match heads, or of the composition, are dried thoroughly over sulphuric acid in a desiccator filled with carbon dioxide, and transferred to a bulb of 25 c.c. capacity blown on the end of a tube 20 cm. long and 15 mm. in diameter. Dry carbon dioxide is introduced, the apparatus evacuated as completely as possible, and the end scaled off. The bulb is then gently heated for two hours at from  $40^{\circ}$  to  $60^{\circ}$ . Phosphorus, if present, will be volatilised, and condensed in the upper part of the tube as a transparent, highly refractive sublimate of octahedral or dodecahedral crystals. It is claimed that this is the most trustworthy test for the presence of small quantities of ordinary phosphorus in the striking compositions of matches containing phosphorus sesquisulphide.

#### C. GERMAN OFFICIAL DIRECTIONS FOR THE EXAMINATION OF MATCHES FOR ORDINARY PHOSPHORUS<sup>4</sup>

The method adopted is less delicate than that of Mitscherlich. The small quantities of ordinary phosphorus present in the red

<sup>1</sup> In recent experiments, E. G. Clayton has observed a very faint luminescence at  $50^{\circ}$ .

<sup>2</sup> *Chem. Centr.*, 1906, 11., 358; *Chem. Weekblad.*, 1906, 3, 367, 404.

<sup>3</sup> *J. Chem. Soc.*, 1909, 95, 440.

<sup>4</sup> *Erlass des Reichskanzlers*, 25th December 1906.

modification are not detected, whereby inaccurate conclusions are avoided.

**I. Introduction.**—The following regulations apply to the examination of:—

1. Red and light red phosphorus, as well as of compounds (mainly sulphides) of phosphorus, which are used in the preparation of match compositions.

2. Match compositions.

3. Matches, as well as other combustible materials. Of the foregoing, match compositions, matches, and other combustible materials, are all to be tested by the methods described under III., and if a positive result is obtained, to be further tested by the methods described under IV.

Red phosphorus is only to be tested for by the methods described under III. In the examination of sulphur compounds of phosphorus, and of light red phosphorus, the methods described under III. are not to be used.

**II. Preparation of the Sample.**—The substance under examination is firstly, as far as is necessary, dried in a desiccator, until on moistening with benzene it can be crushed up, so far as the avoidance of any danger of explosion will allow. In the case of matches, it is usually unnecessary to dry in a desiccator. The match composition is carefully scraped off with a knife; if this be impossible, owing to the inflammability of the composition, the heads are cut off, as closely as possible. The substance thus prepared is boiled with benzene for half an hour under a reflux condenser on a steam-bath. In the case of phosphorus and its compounds, 3 g. are taken and 150 c.c. of benzene; for match compositions 3 g. and 15 c.c. of benzene; and in the case of matches, 3 g. of the scraped heads, or 200 of the cut-off heads and 15 c.c. of benzene. The resulting solution, which contains all the white phosphorus, is filtered when cold, and used for the following tests.

**III. Test with Ammoniacal Silver Nitrate.**—One c.c. of the benzene solution is added to 1 c.c. of an ammoniacal silver nitrate solution, which is made by dissolving 1.7 g. of silver nitrate in 100 c.c. of ammonia, of sp. gr. 0.992.

If, after the two solutions have been thoroughly shaken up and allowed to separate, no change, or only a pure yellow coloration of the aqueous solution is visible, the absence of white phosphorus may be concluded. The colour should be judged directly after shaking and re-separation, and not after continued standing.

If, however, the aqueous solution is coloured red or brown, or contains a black, or blackish brown precipitate, the presence of white or light red phosphorus, or of sulphur compounds of phosphorus, is shown. If red phosphorus is being examined, and the reaction is



negative, white phosphorus is absent, and no further test is necessary. In every other case, the remainder of the benzene solution is treated as follows.

**IV. Luminescence Test for the presence of Ordinary Phosphorus.**—A strip of filter paper 10 cm. long and 3 cm. wide is dipped in the benzene solution, and the excess of solution allowed to drip back. The paper is then fastened to a wire hook attached to a cork, which fits into a glass tube 50 cm. long, and 4.5 cm. in diameter. This tube

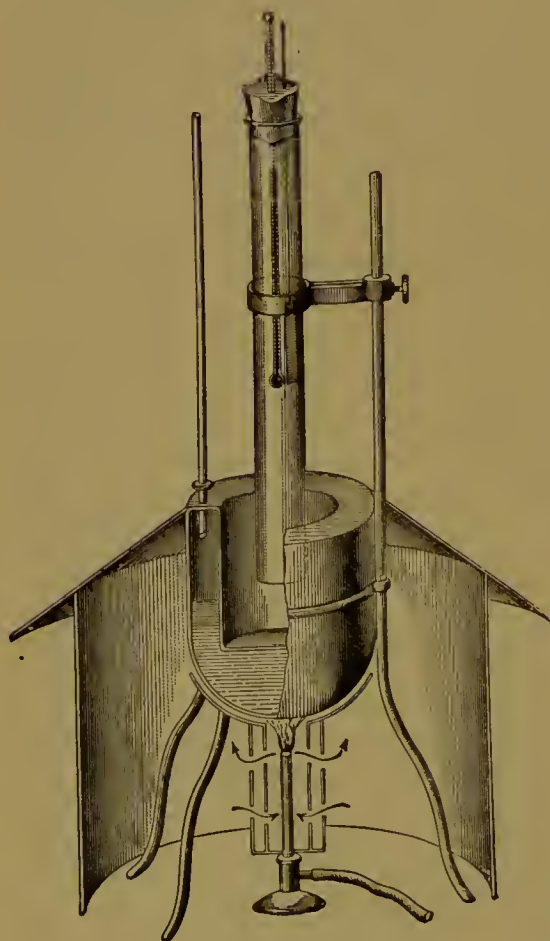


FIG. 79.

is clamped vertically, so that the lower end is 3 cm. inside the 10 cm. wide inner chamber of a Victor Meyer drying oven. A thermometer is so fixed in the cork at the upper end of the tube, that the mercury bulb is 20 cm. from the lower end of the tube. The oven is filled with water, which is heated by a Bunsen or other burner, protected in such a manner, that it throws as little light as possible into the room. The whole heating apparatus is surrounded by a cylinder of blackened tin, which carries a shade of blackened tin; this prevents vertical and horizontal rays of light passing into the room. The arrangement of the apparatus is shown in Fig. 79. On inserting the cork that carries the paper, care must be taken that the paper does not touch the sides of the tube, and that the tube is not moistened by the benzene. The cork carrying the thermometer

and the paper has four cuts down its sides, so that air can circulate freely in the tube. The temperature of the current of air, during the experiment, should be from  $45^{\circ}$  to  $50^{\circ}$ ; this can be regulated by lowering or raising the glass tube in the inner chamber of the heating apparatus. Under no circumstances should the temperature inside the glass tube rise above  $55^{\circ}$ .

The test must be carried out in a darkened room, and care must be taken that no rays, either from outside or from the burner, reach the eye.

It is furthermore necessary to accustom the eyes to the darkness

for some minutes, before beginning the test, as otherwise the luminescence will not be noted with the necessary certainty. The operations before beginning the test are best carried out by the help of a weak source of light, placed at the side of the operator. It is important that all these points should be observed.

Before the actual test, a test should be carried with a solution containing 1 mg. of phosphorus in 10 c.c. of benzene, to see that the apparatus is in good working order; care should be taken that the prescribed temperature is not exceeded.

After the apparatus has been carefully cleaned, the actual test is carried out.

If, after two or three minutes, the strip of paper becomes luminous, white phosphorus is present. The luminosity, as a rule, begins at the ends of the paper, and spreads to the centre. If larger quantities of phosphorus are present, equivalent to 1 mg. in 10 c.c. of benzene, or more, the luminosity increases, and after a short time luminous clouds begin to rise from the paper up the tube. Sometimes serpentine lines of light begin to move from the bottom, top, or sides of the paper towards the centre, and after a short time the whole strip of paper becomes luminous. The luminous clouds appear also, but in this case slightly later.

If, after two or three minutes, no luminosity appears, the test is continued for a few minutes more, and should there be still no luminosity at the end of this time, the absence of white phosphorus is indicated. At the end of the test, a note of the temperature must be taken, and if it was over  $55^{\circ}$  when the luminosity appeared, the test must be repeated; this also applies, if the result is uncertain, or if the luminosity appeared too late.

**V. Test for the presence of Compounds of Sulphur and Phosphorus.**—If the test with ammoniacal silver nitrate gave a positive result, and if there is any reason to test for compounds of phosphorus and sulphur, whether the result of the luminosity test was negative or positive, the following test is to be made:—

One c.c. of the original benzene solution is treated with 1 c.c. of twice normal lead nitrate solution, and well shaken. If, after allowing to stand, a brown coloration is observed where the two liquids meet, or if a black or black-brown precipitate of sulphide of lead is formed, compounds of sulphur and phosphorus are present.

If the test with ammoniacal silver nitrate gave a positive result, but the tests under IV. and V. were negative, light red phosphorus is present.

#### D. TESTS FOR CYANOGEN COMPOUNDS

When soluble cyanides or ferro- and ferricyanides are distilled in the presence of potassium chlorate, with sulphuric acid, free hydrocyanic acid is found in the distillate; insoluble substances of this

nature, such as Prussian and Turnbull's blue, and "the spent oxide" of gasworks are also decomposed. Accordingly, when testing for cyanogen compounds, 1 g. of the scraped match heads are treated with 50 c.c. of warm water and filtered, and both the filtrate and the residue distilled separately with dilute sulphuric acid. Hydrocyanic acid can be identified in the distillate by the following reactions:—

1. *Prussian Blue Reaction*. To the distillate is added a drop of ferric chloride, and a drop of ferrous sulphate solution, or only a drop of ferrous sulphate solution, as this generally contains a little of the ferric salt; this is then made alkaline with a little sodium or potassium hydroxide, well shaken, and carefully acidified with hydrochloric acid. In the presence of hydrocyanic acid, a precipitate of Prussian blue is formed, or the liquid turns green and deposits blue flakes on standing.

2. *Thiocyanate Reaction* (Liebig). Another portion of the filtrate is evaporated on the steam-bath with sodium or potassium hydroxide and a little yellow ammonium sulphide; any hydrocyanic acid present is converted into sodium or potassium thiocyanate, which, when taken up with water and a little hydrochloric acid, gives a deep blood-red coloration on the addition of a drop of ferric chloride.

3. *Nitroprusside Reaction* (Vortmann<sup>1</sup>). To another portion of the distillate a few drops of potassium nitrite are added, then two to four drops of ferric chloride, and enough dilute sulphuric acid to convert the yellow-brown colour into pale yellow. The liquid is heated until it just begins to boil, cooled, a little ammonia added (enough to precipitate the excess of iron), and filtered. Two drops of dilute, colourless, ammonium sulphide are then added to the filtrate; a violet coloration, changing to blue, green, and yellow, shows the presence of hydrocyanic acid. Very small quantities give only a bluish green or a greenish yellow coloration. This reaction is the reverse of the well-known nitroprusside test for sulphuretted hydrogen and alkaline sulphides, and is based on the conversion of any cyanogen present into potassium nitroprusside,  $K_2Fe(NO)(CN)_5$ , which is a very delicate reagent for alkaline sulphides.

4. *Silver Nitrate Reaction*. The distillate is treated with nitric acid and silver nitrate; the presence of hydrocyanic acid is shown by a white precipitate, which should be stable to the light, and readily soluble in ammonia and potassium hydroxide.

5. *Iodide of Starch Reaction* (Schönbein-Kobert<sup>2</sup>). If some of the distillate be added to about 1 c.c. of starch solution, coloured blue by a trace (about 0.04 mg.) of iodine, decolorisation takes place, if hydrocyanic acid is present. This reaction is based on the fact

<sup>1</sup> *Monatsh.*, 1886, 7, 416.

<sup>2</sup> R. Kobert, *Über Cyanmethämoglobin und den Nachweis der Blausäure*, Stuttgart, 1891.



that hydrocyanic acid and iodine give cyanogen iodide and hydriodic acid.

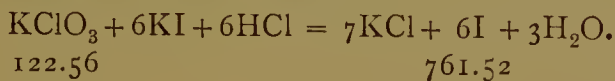


The reaction is very sensitive, and hydrocyanic acid can be detected even in extreme dilution, but it should be noted that iodide of starch is also decolorised by many other substances, such as aluminium and magnesium sulphates, alkalis, sulphur dioxide, carbon bisulphide, carbon oxysulphide, arsenious acid, stannous chloride, uric acid, albumin, and especially by sulphuretted hydrogen.

### E. QUANTITATIVE ANALYSIS OF MATCH COMPOSITIONS

The composition, without any previous softening with water, is carefully separated from the splints, with a sharp knife, care being taken to remove as little wood as possible, and weighed. Or, the weight of the head can be estimated by drying several cut-off match heads in a desiccator over sulphuric acid, and weighing them, then removing the heads with warm water, and drying and re-weighing the pieces of wood.

The estimation of free, white phosphorus is carried out, as described on p. 560, and that of the other constituents by the usual methods. For the estimation of potassium chlorate, 0.5 g. of the composition is washed several times with 50 c.c. of water, a little iodide of potassium (free from iodine) added, and one and a half times the volume of fuming hydrochloric acid. The whole is heated in a closed bottle for fifteen to twenty minutes on the steam-bath, and when cold, the liberated iodine titrated with *N*/10 sodium thiosulphate. The content of potassium chlorate is calculated from the equation:—



## VII.—PHYSICAL TESTS

### A. INFLAMMABILITY ON STRIKING SURFACES

Swedish and other safety matches are supposed to strike only on the prepared surfaces on their boxes, but as a matter of fact they will ignite on several striking surfaces, such as hard wood, smooth hard paper, fine grained and not quite smooth stones, glass, porcelain, etc.

For tests carried out in Germany,<sup>1</sup> the following materials were used:—A smooth board of beech wood 40 cm. long, a sheet of glass 40 cm. long, hard paper, the width of a match-box striking surface, 10 cm. and 20 cm. long, a fine grained plate of marble 15 cm. long, a slightly rough iron plate 15 cm. long, rough glass paper 5 cm. long,

<sup>1</sup> *Arbeiten aus dem Kaiserlichen Gesundheitsamt.*

and fine grained glass paper 10 cm. long. To apply the test, the match is drawn slowly over the surface with an even, gentle pressure.

#### B. TEMPERATURE OF IGNITION<sup>1</sup>

To ascertain the exact temperature at which matches will ignite is extremely difficult, on account of the various necessary precautions, and because concordant results are not obtained when the work is carried out under the same conditions. The temperature at which they will inflame of their own accord, in the case of white phosphorus matches, for instance, is lower as the percentage of phosphorus rises, and is more or less dependent on the distribution of the phosphorus in the composition. The more evenly the phosphorus is distributed throughout the composition, the higher will be the temperature of ignition; should a match head contain a fairly large piece of phosphorus, it is possible for the temperature of ignition to be very little above that of phosphorus. On the other hand, it is known that, by continued careful heating in a current of air at about 70°, many kinds of matches lose their phosphorus, so that although the matches keep their shape and appearance, they are either almost unignitable or the temperature of ignition is found to be much higher than the real ignition temperature. Moreover, the temperature of ignition is higher, the better the matches have been varnished. The ignition point of badly varnished matches varies with the thickness of the coating. The temperature of ignition of any one class of goods can accordingly vary with the circumstances and with the methods of testing employed. A large number of tests should, therefore, be made, and an opinion given with very great care.

The apparatus used in Germany<sup>2</sup> consists of a double-walled, asbestos-covered aluminium box with a double-walled door, provided with a small pane of mica for the purpose of observation. It is provided with three tubes for thermometers, and for inserting the matches, which can be placed at any height inside the box. The apparatus is divided longitudinally inside into three sections by pieces of wire gauze, in the central one of which is placed the thermometer, and in the side ones, the matches for testing. The wire gauze serves to protect the thermometer, as well as the neighbouring matches, from pieces of match composition which may fly off from matches which ignite at a lower temperature. The apparatus is heated by a regulated rose-burner.

Another form of apparatus consists of a glass vessel with a copper lid, in which four springs are arranged for carrying test tubes. The thermometer can be inserted in the centre of the lid. The vessel is filled to about one-third with pure liquid paraffin. A copper wire

<sup>1</sup> Cf. Wiederhold, *Z. für Zündwarenfabrikation*, 1895, No. 280; K. Fischer, *Arbeiten aus dem Kaiserlichen Gesundheitsamt*, vol. xix., p. 318.

<sup>2</sup> Cf. K. Fischer, *loc. cit.*

stirrer passes through the lid. The matches to be tested are hung on the ends of copper wires in the test tubes.

This apparatus is similar to that described by O. Guttman for explosives (*cf.* this Vol., p. 513).

In testing sulphur matches and wax matches, the sulphur or wax should first be removed, as the wax in every test, and the sulphur when the temperature becomes too high, will melt, and enclose the match head.

The determination of the ignition temperature can also be carried out by the method devised by Leyque and Champion.<sup>1</sup> A copper rod, which is to be heated at one end, has at the other end indentations, 10 cm. apart; these concavities or holes are filled with oil or with d'Arcet's alloy (sometimes called Newton's alloy), consisting of 8 parts of bismuth, 5 parts of lead, and 3 parts of tin, and melting at 94°.5. The rod is provided with six holes, and has a length of about 70 cm. from the first hole. Thermometers are inserted in the holes, and that point on the rod is found at which the match composition will ignite. This method is less exact and more troublesome than that of Fischer.

The apparatus employed by Bein to determine the inflammability of gunpowder<sup>2</sup> can also be used.

Horsley<sup>3</sup> uses an oil-bath provided with a thermometer, on which floats a dish containing the substance to be examined. The oil-bath is heated until ignition takes place. The temperature is then read at once and taken as the temperature of ignition. The results are not very exact, as by slow heating phosphorus and sulphur are volatilised; and even if the oil-bath be first brought nearly to the supposed temperature of ignition, and the porcelain dish with the composition is then introduced, there is still the disadvantage that it is necessary to use several oil-baths.

### C. BEHAVIOUR UNDER PERCUSSION

K. Fischer<sup>4</sup> recommends a method by which the results can be expressed in figures. He uses a striking apparatus, consisting of an oak block, partly filled with lead, and protected beneath by an iron plate; this runs in two iron grooves, from a height that can be varied, and falls on to an iron plate on which the match is placed. The height of fall, multiplied by the weight of the block, gives the force necessary to ignite the match in kilogram-metres. The height of fall is 1 metre; the weight of the block can be increased as desired by addition of lead. The greatest weight of the block is 1.5 kg., so that the largest amount of

<sup>1</sup> *Comptes rend.*, 1871, 73, 1478.

<sup>2</sup> *Cf.* Bujard, *Leitfaden der Pyrotechnik*, Stuttgart, 1899, p. 136.

<sup>3</sup> *Cf.* Fehling-Hells, *Handwörterbuch der Chemie*.

<sup>4</sup> *Arbeiten aus dem kaiserlichen Gesundheitsamt*, vol. xix.



work which the machine can do is 1.5 kg.-metres. The results are not very accurate, as several circumstances, friction, for example, are not taken into account. However, as these errors are the same in each test, the results are comparative. The sensitiveness of one and the same class of matches under percussion varies very widely. Matches of the same class with large heads ignite more readily than those with small heads. In general, the scraped-off composition is more easily ignited than the match, so that in forming conclusions from this test as much care must be exercised as in judging the temperature of ignition.

#### D. SENSITIVENESS TO MOIST AIR

To test this property the matches are placed in a vessel over wet cotton wool, and the vessel then placed under a bell-jar over a vessel of water. Observations are made with regard to the behaviour of the matches when moist, their durability, appearance, stickiness, and the like.

#### E. BEHAVIOUR WHEN TREATED WITH CONCENTRATED SULPHURIC ACID BY MOISTENING OR BY IMMERSION

Observations are made as to whether inflammation of the match head takes place with this treatment.

### B.—PRIMINGS AND FIREWORKS

Fireworks, so far as their active contents are concerned, are derived from a comparatively small number of components or mixtures (firework mixtures).

These comprise, on the one hand, easily combustible substances, such as charcoal, sulphur, antimony sulphide, resins, and tar; and on the other hand, they include substances which readily give up oxygen and support combustion, such as saltpetre (potassium nitrate), and potassium chlorate or other chlorates. A third category includes those substances used for the various colour effects (barium, strontium, copper, and other salts), and also finely divided metals, and coarse particles of charcoal, to cause sparks and showers of fire ("golden rain," and the like).

#### I.—FIREWORK COMPOSITIONS

The following substances form the groundwork of most firework compositions:—Gunpowder (grain powder and meal powder), saltpetre and sulphur, charcoal mixture, and grey mixture.

## A. GUNPOWDER

Ordinary coarse-grained gunpowder (grain powder) is used for impulsive or percussive charges (for throwing fireworks from bombs, mortars, etc.), or for explosions; the coarse-grained powder is necessary in these cases, as quick combustion and a rapid evolution of gas is required.

Further, meal powder, that is to say, a finely powdered blasting powder, is used; that employed by makers of fireworks is of varying composition. For instance, a blasting powder is used, which, powdered and passed through a 0.5 mm. mesh sieve, consists of:—

60.2	parts by weight of doubly refined potassium nitrate,
18.4	„ „ of sulphur,
21.4	„ „ of alder wood charcoal,

and explodes at 20° by Wagner's powder test.<sup>1</sup>

An ordinary blasting powder, consisting of 70 parts of saltpetre, 18 parts of sulphur, and 12 parts of charcoal is suitable. As a matter of fact any ordinary gunpowder can be converted into meal powder, as its strength can easily be modified by the proportions of the ingredients. Meal powder is used when slow combustion is necessary. The qualitative and quantitative tests are carried out as detailed under black powder (this Vol., p. 495).

*Wagner's Powder Test.* In various factories, where fireworks are made, it is necessary, for some of the mixtures and for the calibre of the cartridges, to use a gunpowder of definite power. Tests by which the power can be estimated are carried out by means of Wagner's apparatus.

This apparatus (Fig. 80) consists of a column, *a*, fastened to a support, which can be levelled by means of screws; *b* is an angular lever, which moves on a hinge at *c*, and carries the counter-weight *e*. The unweighted arm *b* carries a small mortar, *d*, and a spring catch, *i*, which moves over a graduated metal arc, *f*. When the powder explodes, the arm is pressed downwards by the force of the explosion, and

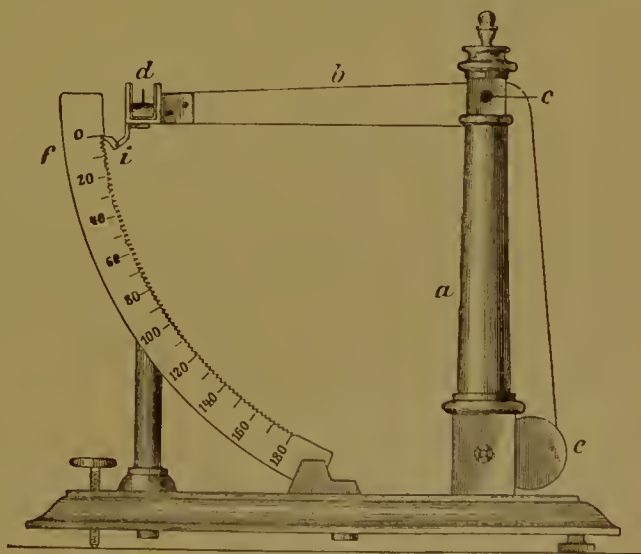


FIG. 80.

<sup>1</sup> Cf. A. Pirker, *Kunstfeuerwerkerei*, 1892.

the distance through which it is displaced is shown by the spring catch. The number of degrees can be read directly from the graduated scale. The charge for each test is 2.2 g. of powder. The results obtained by this method are not very accurate, owing to the large size of the mortar, and the smallness of the charge; it is, therefore, necessary to repeat the test several times, and to take the mean of the results.

#### B. SALTPETRE AND SULPHUR

This is a mixture of 3 parts of nitre with 1 part of sulphur, and contains approximately equivalent weights of the two components. When this mixture, which yields very little gas, is burnt, the products formed are mainly potassium sulphate, sulphur dioxide, and nitrogen, in accordance with the following equation:—



This mixture is the basis for most compositions which are to give light, and also for grey mixture.

#### C. GREY MIXTURE

This is made by mixing 7 parts of meal powder with 100 parts of saltpetre and sulphur, and is mostly used for the manufacture of fire-balls (used in war).<sup>1</sup> These consist of twill bags, charged with compressed grey mixture, which is filled into them with the aid of spirit; they are fired by means of a composition fuse. Grey mixture mixed with antimony sulphide is used for torches.

This material can be tested in the same manner as gunpowder (*cf.* p. 495).

#### D. CHARCOAL MIXTURE

This name is given to meal powder, of which 500 parts are mixed with 6 to 8 parts of charcoal. To this class also belong the slow mixtures or slow fires, which consist of meal powder, the explosion of which is more or less retarded by additions of charcoal. Further, there are quick and slow squib mixtures, also so-called "green" mixtures, which are made up of various kinds of slow mixtures. The green mixtures contain larger proportions of sulphur. In addition there are propelling mixtures, which consist of meal powder, nitre, and charcoal (sometimes a little chlorate of potash), and spark mixtures, similar to the last, consisting of nitre, sulphur, and charcoal. The former are used for war rockets, and the latter for firework rockets. It is necessary that these mixtures should evolve large quantities of gas, and they are, therefore, made with a meal powder to which charcoal has been added. An old Prussian prescription for war rockets is as follows<sup>2</sup>:—Thirty-two

<sup>1</sup> *Cf.* Bujard, *Leitsaden der Pyrotechnik*, 1899, p. 16.

<sup>2</sup> *Cf.* Busch-Hoffmann, Bolley's *Handbuch d. chem. Technik*, vol. vi., p. 384.



parts of nitre, 12 parts of sulphur, 32 parts of meal powder, and 16 parts of well-powdered charcoal. Other mixtures are as follows:—

Meal powder . . . . .	8 parts
Coarsely powdered charcoal . . . . .	9 „
or Nitre . . . . .	16 „
Charcoal . . . . .	3 „
Sulphur . . . . .	4 „

Hence it is apparent that the charcoal mixture can be used, as these are very similar to the spark mixtures, which consist of:—

Nitre . . . . .	12 or 16 parts
Sulphur . . . . .	3 or 4 „
Charcoal (coarse) . . . . .	5 or 9 „

Spark mixtures are used for cases, constricted at one end, which can be suitably grouped and mounted, so as to be used for cascades of fire, suns, fans, palm trees, fixed stars, and various other kinds of fireworks. These mixtures are also made up with additions giving a reddish light, and with metal filings; those containing metals are known as “brilliant mixtures.”

Such mixtures are analysed similarly to gunpowder. For tests for potassium chlorate, see Vol. I., p. 517; and for the examination of the various ingredients, nitre, charcoal, and sulphur, see this Vol., pp. 482, 486, and 487. The same points must be noted in judging these substances as in the case of matches.

## E. ILLUMINATION AND COLOURED FIRE MIXTURES

In addition to the substances already mentioned, these contain, almost invariably, potassium chlorate, together with substances such as strontium or barium nitrate, for producing the colours. They are accordingly mixtures of combustible substances with compounds which give coloured flames, and, like exploding gunpowder, they throw off small particles which continue to burn while in motion, and owe their power of projection to the combustion. At first sight, it would appear easy to make one of these mixtures, but several factors have to be taken into account, such as the velocity of combustion, which in the case of “stars” should be great, for coloured lights slower, and for flames slowest of all; the temperature at which the colour-imparting substance will act best; the formation of slags, and their fusibility. To find out whether these substances are suitable for colour mixtures, they should be thrown, in the form of a dry and very fine powder, into flames of varying temperatures such as hydrogen flames, the temperature of which has either been raised by oxygen, or lowered with nitrogen, so as to find out the effect of different temperatures. But this test is not always successful, as in the case of lithium salts, which although they

impart an intense carmine coloration to flame, do not produce a colour of anything like the same intensity in mixtures. The manufacturer mostly tests this by making a small sample mixture,<sup>1</sup> consisting of:—

Potassium chlorate	.	.	.	.	20 parts
Sulphur	.	.	.	.	5 „
Gum mastic	.	.	.	.	1 „

If the substance to be tested gives a good fire coloration with this mixture, it can probably be used.

The following formulæ have been found upon actual trial to yield satisfactory green and red colour mixtures respectively (E. G. Clayton):—

	Green.	Red.
Barium nitrate	60	...
Strontium nitrate	...	63
Potassium chlorate	15	18
Sulphur	13	13
Realgar	11	...
Shellac	...	5
Charcoal	1	1
	<hr/> 100 <hr/>	<hr/> 100 <hr/>

By mixing together combustible compositions, which give different colours, a tint is obtained, which is nearer to a white than to a mixture of the two colours. On mixing red and yellow, a pale orange results; blue and yellow give a not very intense pale green; blue and red give violet, and this is the only good colour obtained by mixing; red and green give white.<sup>2</sup>

#### F. POTASSIUM CHLORATE AND SULPHUR

This consists of a mixture, used for adding to illumination mixtures, of 125 parts of potassium chlorate and 35 parts of sulphur; potassium perchlorate can be substituted for the chlorate.

#### G. "COLD" AND "WARM" MIXTURES

If the components are simply mixed together, the mixtures are known as "cold" mixtures. "Warm" mixtures are those made by fusing the substances together. The following is a "warm" mixture:— Grey mixture, 85 parts; meal powder, 29 parts; and antimony sulphide, 5 parts. This is used for fire balls and for white fire. Bengal lights are also often made by fusion.

<sup>1</sup> Cf. *Dingl. polyt. J.*, 1851, 119, 203.

<sup>2</sup> For further particulars, see Bujard, *Pyrotechnik*, 1899.

## H. MIXTURES FOR IGNITION PURPOSES

These are for the purpose of firing inflammable objects at a distance. They must be made in such a manner as to combine the property of burning slowly with the development of as high a temperature as possible. The mixture used in Prussia for this purpose consisted of 76 parts of grey mixture and 24 parts of colophony. In Bavaria, a combination of meal powder with "warm" mixture was customary.

## I. MIXTURES FOR SPECIAL FIREWORKS

The following mixtures are used. For fuses, a mixture of meal powder, charcoal, and mica; for "golden rain," meal powder, charcoal, and iron filings; for "silver rain," lead nitrate, potassium nitrate, and charcoal; for "comets," a little meal powder and charcoal. Picric acid mixtures were introduced by Dessignolle and Castela<sup>1</sup>, by Brugère,<sup>2</sup> and by E. Jacobsen, for causing detonations with coloured fires.

The first named used ammonium picrate together with barium nitrate, strontium nitrate, etc.; the latter used the picrates of strontium and barium, which, however, have to be fired by means of a fuse. These mixtures are best made by the manufacturer himself from picric acid and the respective carbonates. For the testing of picric acid, see this Vol., p. 508.

Whistling squibs are made with magnesium picrate. The mixture is prepared according to the formula of the inventor, Weiffenbach, of Stuttgart. Two hundred grams of picric acid and 800 g. of nitre are dissolved in hot water, and saturated with 30 g. of magnesium carbonate, and the precipitated crystals then dried.

## K. MERCURY FULMINATE (HOWARD'S SILVER)

This is used for percussion caps, either alone, or mixed with other combustible substances, or with gunpowder, potassium chlorate, nitre and sulphur, etc. These additions serve the purpose of retarding the decomposition, and of increasing the volume of the gases formed. Percussion caps are made of thin, rolled copper sheet. The following is a prescription for this mixture:—One hundred parts of mercury fulminate are rubbed into a paste with 30 parts of water on marble slabs with boxwood rubbers; to this are added 50 parts of nitre, or 62.5 parts of nitre and 29 parts of sulphur. The paste is dried on sheets of paper, and granulated by means of hair sieves. Some makers, after placing the grain in the percussion cap, cover it with a small copper plate, while others coat the grain with mastic varnish. Discs of varnished tinfoil, or paper, or of both together, are sometimes used (E. G. Clayton). One

<sup>1</sup> Cf. G. Schultz, *Steinkohlenteer*, p. 456.

<sup>2</sup> *Zeit. f. Chem.*, 1869, p. 667.



kilogram of mercury, after conversion into the fulminate, is sufficient for 40,000 percussion caps.

*Analysis of Mixtures, containing Mercury fulminate.* F. W. Jones and F. A. Wilcox<sup>1</sup> advise, in the case of a mixture containing potassium chlorate, the fulminate, and antimony sulphide, to first extract the fulminate of mercury from a weighed quantity, by means of a solution of ammonia in acetone, then the chlorate with water, and to weigh the residual antimony sulphide.

H. Brownsdon<sup>2</sup> estimates the mercury fulminate by decomposing it with excess of sodium thiosulphate, and determining the resulting alkalinity by *N*/10 sulphuric acid, previously standardised against especially prepared pure fulminate.

The explosive properties of fulminate of mercury have been studied by Berthelot and Vieille, who give the following equation for its decomposition:—



When mixed with 30 per cent. of water, it can be rubbed on a marble slab, with a wooden rubber, or a soft, clean cork, without any danger.

The following are the results, in round numbers, of a series of analyses of several kinds of percussion caps, in one of which lead thiocyanate had been used instead of mercury fulminate (E. G. Clayton):—

	1.	2.	3.	4.	5.
Mercury fulminate . . .	33	21	25	27	...
Lead thiocyanate . . .	...	...	...	...	36
Antimony sulphide . . .	15	45	34	...	...
Sulphur . . . . .	...	...	...	7	...
Ground glass . . . . .	...	...	18	43	...
Potassium chlorate . . .	52	34	23	23	64
	100	100	100	100	100

G.

G.

G.

G.

Approximate weight of charge

per cap . . . . . 0.025    0.046    ...    0.022    0.025

In these analyses, Brownsdon's method was employed for the determination of the fulminate, the antimony was estimated volumetrically, the lead gravimetrically, and the thiocyanic acid by a colorimetric method; the figures for potassium chlorate were obtained by difference.

<sup>1</sup> *Chem. News*, 1896, 74, 283.

<sup>2</sup> *Ibid.*, 1904, 89, 302.

## II.—PRIMINGS

## A. THE FIRING-EXCITER

This consists of a mixture of meal powder and alcohol. A fast exciter consists of 1000 g. of meal powder and 570 c.c. of alcohol; a slow exciter of 1000 g. of meal powder and 720 c.c. of alcohol. These mixtures are best made with the hands in a copper pot, or in a porcelain basin. The exciter is painted on to the quick match at the firing hole where the paper of the covering of the firework has been twisted together, for instance where the fuse is fastened to crackers and squibs. In general, all those places which are intended to catch fire are painted with this mixture. If it is intended to stick tightly, a solution of 16 g. of gum-arabic in 140 c.c. of water is added. The tests used are similar to those employed for gunpowder (*cf.* p 495).

## B. SLOW AND QUICK MATCHES, FUSES

Triple and quadruple cotton threads, purified from grease as in the case of guncotton, are soaked in quick firing-exciter, and sprinkled with meal powder. After the impregnation, they are allowed to lie for six to eight hours, then rolled on a bobbin, and passed through a board, provided with holes of various sizes, so as to impart the required strength and uniform thickness to the threads, after air-drying. They are again passed through the firing-exciter, which has been thickened with gum-arabic, then again through the holes in the board, sprinkled with meal powder, and dried; finally they are wrapped in paper, placed in dry boxes, and stored in a dry place. According to the formula used for the Prussian artillery, the following quantities are necessary for a fuse 100 metres long, and 0.52 cm. in diameter:—2.94 kg. of meal powder, 4.35 litres of alcohol, 21.2 g. of gum-arabic, and 0.24 kg. of cotton thread. Thus prepared, the speed of burning is 1 metre in twenty-four seconds.

Better fuses are obtained by a previous treatment of the cotton with a special mordant (*cf. infra*).

In the case of a *train of powder* (or *leader*) the fuse is covered. These covered fuses protect the firework against pre-ignition, and also cause a quicker firing. For this purpose the fuses are covered with paper tubes.

*Quick Matches* or *Paper Fuses* are also enclosed in paper and are, as a rule, about 28 cm. long, and 0.33 to 0.21 cm. in diameter.

*The Mordant for Fuses* serves in the first place to make the fuse more inflammable, and secondly, to ensure a steady and quiet combustion, for instance, as in the case of time fuses. The mordant consists

of a solution of 1 part of nitre in 10 parts of water. The dry cotton threads are allowed to remain in this solution for twelve hours, and are then wrung out and dried.

*Slow Matches*, as prepared for pocket match boxes, are obtained by boiling loosely spun cotton in a solution of lead nitrate, consisting of 1 part of lead nitrate in 10 parts of water; they are then allowed to dry in the air without being wrung out. Another method consists in boiling the cotton in a solution of lead acetate (1 part of lead acetate in 20 parts of water) and when dry, placing them in a solution of 1 part of potassium bichromate in 10 parts of water. The resulting threads are yellow, owing to the formation of lead chromate.

*Fuse paper*. In dry weather this can be used in place of the ordinary fuses, and finds general use for certain firings. It is made by spreading firing-exciter on to both sides of sheets of blotting paper, sprinkling it with meal powder and drying it.

#### C. GUNCOTTON FUSES

The preparation of guncotton fuses is exactly the same as that of guncotton. They can be tested as is described in Vol. I., p. 136, and in the section on "Explosives" (this Vol., p. 496). These fuses transmit fire faster than any other form, and are mostly used for firing large set-pieces; they burn very fast, and will fire a fuse-paper wrapped round them with absolute certainty; they have the further advantage that they can be used in wet weather.

#### D. PORT-FIRES

These are fireworks which will cause the firing of charges and of other fireworks quickly and safely in cases where the fuse cannot be used. Port-fires must, therefore, be capable of burning very well, and must not be put out by even the strongest shower of rain. The mixtures employed must be very rich in oxygen, and it is recommended to fuse together the nitre and sulphur mixture used in their manufacture.

Port-fires are about 40 to 50 cm. long, and should give a flame 8 mm. long. The necessary casing is made of strong cardboard, and is soaked in a solution of nitre so that it should burn easily; the diameter is about 1 cm. The mixture is filled into these cases, about 5 cm. deep at a time, and slightly compressed: sometimes it is moistened with linseed oil. The composition of some typical port-fires is as follows:—

<i>Prussian Mixture.</i>				<i>French Mixture.</i>			
Nitre and sulphur . . .	100	parts		Nitre . . . . .	6	parts	
Colophony . . . . .	7	"		Sulphur . . . . .	3	"	
Meal powder . . . . .	85	"		Meal powder . . . . .	1	"	



*Swedish Mixture.*

Nitre . . . . .	24 parts
Sulphur . . . . .	14 „
Meal powder . . . . .	11 „
Colophony . . . . .	1 „

## E. COMPOSITION FUSES

These are really only port-fires on a smaller scale; they are fastened to fireworks and effect a certainty of firing. They are made of strong paper, have a diameter of 0.5 cm. and a length of from 6 to 8 cm. They are filled up to 2 to 3 cm. with meal powder, on the top of which a layer of priming-mixture is placed. Such mixtures consist of:—

*Prussian Mixture.*

Nitre and sulphur . . . . .	100 parts
Meal powder . . . . .	25 „

The mixtures used for time-fuses can also be employed.

## F. TIME-FUSES

Many fireworks (set-pieces) can only be successful, and produce the desired effect, if some parts, such as torches, squibs, etc., have a definite time for burning. Time-fuses are used for exploding charges, or for igniting fireworks in a definite period of time. These time-fuses are tubes filled with a mixture in such a manner that a certain length will burn in a definite time.

As in the case of igniters, the differences in the action of time-fuses are based solely on the proportions of a few constituents (powder, nitre, sulphur, etc.), and upon the density of the mixtures. Their examination is conducted as described above. The main requirement in the case of these fuses is to determine the time of burning.

## III.—THE DURATION OF BURNING

In the case of fireworks, the maintenance of a definite duration of burning is especially necessary, where set-pieces are used, or where rotations are required and the like. It is less necessary in the case of rockets, when they are to be let off together in the form of a fan, etc., or in the case of a quantity of squibs, because the composition and compression of the mixtures used are sufficient to regulate the combustion. The duration of burning of a mixture is dependent upon:—

1. The composition.
2. The degree of dryness.
3. The degree of fineness, and the thoroughness of mixing.
4. The degree of compression.
5. The area of its burning surface.
6. The area of the delivery opening.
7. The nature of the covering.

From this it is obvious that successful results can only be obtained by working with uniformly made mixtures, with the same covering material, and uniform charging. Small divergences nevertheless occur, but these can be neglected, as they make no difference, when the firework is ignited. Moisture in the mixture retards the firing, not only directly by its presence, but also because it causes decomposition, mainly between the sulphur and the metals in the mixture, when the fireworks are stored. The area of the delivery opening retards the firing when it is less than  $\frac{1}{5}$  to  $\frac{1}{6}$  of the area of the case.

The duration of burning is determined with a stop-watch, and is of importance in the case of set-pieces, in which several kinds of mixtures are present. In this case the time can be regulated, by regulating the depth of the mixture in the cases; shorter cases for slower mixtures, and longer cases for quicker mixtures, can be used.

#### IV.—TESTING FIREWORK MIXTURES FOR LIABILITY TO SPONTANEOUS COMBUSTION

Examples of compositions, having pyrophoric properties, used in the manufacture of fireworks, are mixtures containing iron filings and sulphur, which have become damp; also certain Bengal light mixtures. Illumination mixtures containing nitrate of strontium or barium, sulphur and potassium chlorate, will often fire of their own accord, after standing for a few hours. This occurs chiefly when the ingredients have been quickly dried before use, and when the mixture is left lying in a warm, moist place. An ignition of this nature can be prevented by making the mixture of pure materials. A better preventive, according to Clarke,<sup>1</sup> is an addition of a small quantity of antimony sulphide or, of a small quantity of sodium carbonate or chalk, as in the case of nitrocelluloses. These latter take up any acid impurities of the sulphur or other components, and form compounds which are inactive with chlorates and nitrates. This treatment is of some use, but the action of antimony sulphide is questionable. Mixtures which have become damp, must be dried separately and with great care, as they ignite easily. Mixtures containing copper oxide also fire readily, but this can be prevented by substituting copper carbonate for the oxide.

Dennstedt's apparatus for the examination of coal,<sup>2</sup> would no doubt serve for the examination of such mixtures as to their liability to spontaneous combustion.

The test proposed by Meischmeier is carried out as follows:—Five grams of the mixture are slowly heated in a dish on a sand-bath, to 100°, and kept at this temperature for two hours. If it is now moistened with water, and again dried, it should not ignite spontaneously.

<sup>1</sup> *Dingl. polyt. J.*, 1867, 183, 164.

<sup>2</sup> *Z. angew. Chem.*, 1908, 21, 1826.

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## CALCIUM CARBIDE AND ACETYLENE

By Professor G. LUNGE, Ph.D., Dr. Ing., and E. BERL, Ph.D. English translation revised by J. T. CONROY, Ph.D., B.Sc., the United Alkali Co., Liverpool.<sup>1</sup>

### A. RAW MATERIALS FOR THE MANUFACTURE OF THE CARBIDE

**1. Coke.**—It is important that this shall be as free as possible from ash, sulphur, and phosphorus. The method of testing is described in Vol. I., pp. 242, 420. Apart from this, it is immaterial whether furnace coke or gas coke is used; the former is, however, generally purer than the latter.

**2. Anthracite.**—This is sometimes used instead of coke, and should be similarly free from the impurities mentioned above. According to J. W. Gatehouse,<sup>2</sup> no carbonaceous material containing more than 5 per cent. of mineral matter is suitable for the manufacture of carbide.

**3. Limestone.**—According to Duparc,<sup>3</sup> limestone intended for the manufacture of calcium carbide should not contain more than 0.02 to 0.025 per cent. of phosphoric anhydride,  $P_2O_5$ , and 2.0 to 2.5 per cent. of magnesia; further, the proportion of silica and silicates must not be too high. Both alumina and manganese are objectionable impurities. The presence of phosphoric acid leads to the formation of calcium phosphide, and thus to the contamination of the acetylene with phosphoretted hydrogen; magnesia reduces the fusibility of the carbide and renders the manufacture more difficult. Further, magnesia, alumina, and manganese yield carbides which on decomposition with water liberate either hydrogen or methane, or a mixture of the two, and thus while they do not necessarily diminish the gas-yield of the carbide, reduce the illuminating power of the evolved gas, since both gases burn with practically non-luminous flames.

For the estimation of small quantities of magnesia in presence of large quantities of lime, Duparc takes 5 to 6 g. of the sample and first removes the lime by dissolving it in acetic acid; the magnesia is then determined in the residue. For the estimation of

<sup>1</sup> Dr Conroy desires to record his indebtedness to Mr J. W. Gatehouse, Chemist to the British Acetylene Association, and to Mr F. B. Gatehouse, Technical Editor of *Acetylene*, for much valuable assistance in the revision of this section.—C. A. K.

<sup>2</sup> *Acetylene*, 1908, 5, 310, 346.

<sup>3</sup> *Chem. Zeit.*, 1904, 28, 688.

the phosphorus, 100 g. of the sample is taken, the lime dissolved in nitric acid, the solution concentrated, nitromolybdate solution added at a temperature of  $50^{\circ}$ , the solution filtered, the precipitate washed with ammonium nitrate, and dissolved in aqueous ammonia. The phosphate is precipitated in this solution with magnesia mixture, large quantities of liquid being avoided, and very small filters being used.

F. B. Gatehouse<sup>1</sup> has described methods for the complete analysis of limestone, coke, coal, and carbon electrodes, so far as the above-mentioned impurities are concerned. From theoretical considerations, he concludes that the permissible limit for phosphorus should not exceed 0.03 per cent.  $P_2O_5$  on the raw materials employed if the acetylene has to comply with the regulations of the British Acetylene Association (0.05 per cent.  $PH_3$  by volume); whilst no standard is fixed for sulphur compounds in acetylene, he is of opinion that the sulphur content of the raw material ought not to exceed 0.05 per cent.  $SO_3$ .

## B. CALCIUM CARBIDE AS A COMMERCIAL PRODUCT

The commercial product contains a series of other compounds besides calcium carbide. Moissan<sup>2</sup> decomposed calcium carbide with sugar solution, so that the lime remained in solution; in the residue (3.2 to 5.3 per cent.) the following compounds were detected chemically and microscopically:—Silicon carbide, sometimes calcium silicide and crystalline silica, calcium and aluminium sulphides, iron silicide, iron silico-carbide, calcium phosphide, and graphite (never diamond).

The occurrence of iron silicide, silicon carbide (carborundum), etc., in commercial calcium carbide, although interesting from a scientific standpoint, is not of importance in the application of carbide to the preparation of acetylene. Hempel and Kahl<sup>3</sup> found in American calcium carbide, 6 to 8 per cent. of carborundum and iron silicide, and 0.2 to 0.24 per cent. of silica. Ahrens<sup>4</sup> found as accidental impurities in calcium carbide, iron silicide, iron silico-carbide, and a silicide of copper and iron; he describes the analytical methods used for their detection.

In the analysis of commercial calcium carbide, the chief consideration is the total yield of gas evolved on treatment with water. The gas is generally assumed to be wholly acetylene, and is calculated as such. As is well known, however, the gas obtained is never pure acetylene; it may contain as much as 4 per cent. of impurities, of which the following are the most important:—Sulphuretted hydrogen, phosphoretted hydrogen, ammonia, carbon monoxide, hydrogen, methane, nitrogen, and oxygen. Only the three first of these are seriously objectionable

<sup>1</sup> *Acetylene*, 1909, 6, 30.

<sup>2</sup> *Comptes rend.*, 1898 127, 457.

<sup>3</sup> *Z. angew. Chem.*, 1898, 11, 53.

<sup>4</sup> *Ibid.*, 1900, 13, 439.

and need be considered in the light of impurities; sulphuretted hydrogen and phosphoretted hydrogen impart a very unpleasant smell to the gas, render it poisonous, and give rise to harmful acid products on combustion. The quantity of calcium sulphide and phosphide in good calcium carbide is very small, since both of these can be almost eliminated by suitable selection of the raw materials. In some cases, however, it may be necessary to ascertain whether the sample consists of good calcium carbide or not.

Ammonia, which occurs only in traces, when not absent altogether, aids in the formation of acetylene compounds of metals and is also detrimental in the purification by chloride of lime.

In regard to calcium phosphide, it is important to bear in mind that phosphoretted hydrogen appears to facilitate the formation of copper acetylides, whilst the presence of larger quantities in acetylene may even render the gas spontaneously inflammable. A case has actually occurred in which calcium carbide gave off a spontaneously inflammable gas immediately on contact with water.

**Sampling.**—According to Lunge and Cedercreutz,<sup>1</sup> the examination of calcium carbide is rendered very much more difficult by the great lack of homogeneity in the lumps which come into commerce. A representative sample must, therefore, be obtained by grinding a large quantity and mixing it well together. This cannot, however, be done in the ordinary way, owing to the very appreciable decomposition which would occur by the action of atmospheric moisture (as evidenced by the smell), during the long time necessary for grinding the hard mass sufficiently fine, and performing the necessary mixing and quartering. The only satisfactory method is, therefore, to break up the carbide quickly into pieces of about the size of peas. These can, of course, be only mixed in a very imperfect manner, and in order to obtain a sample which can in any way be regarded as representative by this procedure, it is necessary to take, at least 50 g., but preferably 100 g., for each determination.

Even by this procedure it is impossible to be certain that a truly average sample has been obtained. This would only be possible if a large sample were taken from different parts of the melt and ground, and mixed together in a closed ball mill, or in some similar apparatus in which the substance was not exposed to the air. (The usual laboratory grinding apparatus would give much too low results, on account of the decomposition occurring during the grinding.) If this were done, it would be sufficient to take quantities of about 10 g. for the analysis, using an ordinary graduated glass gasometer, since the quantity of gas evolved would not be much more than 3 litres. It would, of course, be necessary to so arrange the mill as to permit of thorough

<sup>1</sup> *Z. angew. Chem.*, 1897, 10, 651.



cleaning and drying for each sample tested. In default of such an apparatus, it is necessary to adhere to quantities of not less than 50 to 100 g., and preferably 250 g.

P. Wolff<sup>1</sup> has expressed very similar views. Especially when the carbide has been produced in ingot form, two samples taken in the immediate vicinity of each other may give very different results. In works which adopt the "tapping process," a sample of each "tap" is taken at once and set aside. Where the carbide is made in ingots, the crust of the ingot is first detached, and the interior broken up, as many separate samples being taken as possible, and then further disintegrated with stone crushers, etc. Carbide treated whilst still hot, can be broken up without suffering much decomposition by atmospheric moisture, more especially at the high temperature prevailing in the works, and samples may safely be taken from material treated in this way. These conditions do not, however, obtain when samples are taken by the buyer or sampler; it is then necessary to take samples from at least one drum in every ten, chosen as uniformly as possible. Each of the selected drums is opened and the contents quickly tipped out; during this process, sample pieces of all sizes are taken from different positions, thrown into a sheet-iron drum standing by, which is closed air-tight and sealed. The pieces are then broken up as rapidly as possible in an iron mortar, with a broad pestle, in the laboratory, and after mixing well, samples of not less than 50 g. and preferably of 250 g. are taken for each separate test.

Odernheimer<sup>2</sup> has pointed out that very erroneous results are obtained if the dust, which collects mainly at the bottom of the drums, is not taken into consideration. All drums, he states, should be completely emptied on to an iron sheet, the contents quickly mixed, and quantities of about 500 g. shovelled out from two separate parts and transferred to cases which are at once sealed. In dealing with larger quantities (10 to 20 tons), it is best to fill a sheet-iron drum provided with a lever or screw-down lid; the contents are then mixed as above, and samples taken and put into tins which can be sealed. When quantities of 100 drums and upwards are to be tested, a sample is taken from every tenth drum, but in sampling smaller quantities a larger proportion should be taken. As explosions occasionally occur in unsoldering the drums, they should only be opened by striking or cutting.

According to the regulations of the British Acetylene Association, one drum must be sampled for each 1 ton of carbide in the consignment. The whole of the contents of the sample drum are emptied on to the dry floor of the sampling room, and portions of at least 1 lb. are taken from points representing respectively the top, middle, and bottom of the

<sup>1</sup> *Z. Calcium Carbid Fabr.*, 3, 243.

<sup>2</sup> *Chem. Zeit.*, 1902, 26, 703.

drum, and stored in an air-tight receptacle. Previous to analysis, the sample so taken (not less than 5 lbs. in all, per drum) is put into an iron mortar and broken down to pieces of from 1 inch to  $\frac{1}{4}$  in. mesh by means of an iron pestle, an indiarubber cover being fitted over the mortar to exclude air as far as possible. The sample is then well mixed and the required quantity weighed off for analysis, after screening to remove the dust produced in the sampling.

The Association allows carbide of standard size—that is, in pieces of 1 in. up to  $3\frac{1}{2}$  ins. mesh—to contain up to 5 per cent. of dust. Should the amount of dust in the sample drum appear excessive, the contents of the drum should be passed through a sieve of  $\frac{1}{8}$  in. mesh, and the dust so obtained weighed.

The German Acetylene Union has adopted the following regulations in regard to sampling. If it is not agreed to send one unopened drum in the case of consignments of less than 5000 kg., and two unopened drums with consignments of 5000 kg. or more, the sampling shall be carried out as follows:—A sample of at least 2 kg. must be taken; if the consignment consists of not more than twenty drums, this sample may be taken from any one drum and from two parts of the drum, the middle, and either the top or bottom. With consignments of more than twenty drums, samples of at least 1 kg. each must be taken from 5 per cent. of the whole. The sampling must be carried out in the presence of a representative agreed to by the contracting parties, and the sample must be taken with a shovel, not by hand, and to avoid local accumulations of dust each drum sampled must be inverted twice before sampling. The samples must be placed at once in one or more closed vessels which are air-tight, and exclude all access of moisture, and are then sealed. If a mutual representative is not agreed upon, the samples are similarly taken by each of the contracting parties.

The regulations of the Austrian Acetylene Union are similar to the above. With consignments of fewer than five drums (about 100 kg.), a sample is taken from one drum, with those of from five to twenty drums from two (about 1 kg. from each), and with those of more than twenty drums from at least 10 per cent. of the whole.

### Determination of the Yield of Gas.

In this country it is customary to grade the carbide into pieces varying in size, according to the use to which the carbide is to be put, and to state the gas yield in cubic feet of gas, measured at 60° F. and 30 in. mercury (15° 5 C. and 760 mm.), per 1 lb. of carbide. The lower grades ranging from pieces of  $\frac{1}{12}$  to  $\frac{5}{8}$  in. diameter, and intended for cycle lamps, etc., are supposed to yield 4.5 cb. ft. of gas per 1 lb. (281 litres per 1 kg.). The higher grades,  $\frac{5}{8}$  to 1 in., for motor lamps, and 1

to  $3\frac{1}{2}$  ins. for acetylene gas plants yield 4.8 cb. ft. per 1 lb. (300 litres per 1 kg.). For pieces less than  $\frac{1}{12}$  in., and for dust no guarantee is given; the gas yield is only approximately 1 to 2 cb. ft. per 1 lb.

According to the regulations of the British Acetylene Association, carbide of standard size—that is, in lumps of 1 to  $2\frac{1}{2}$  ins. or larger—should yield not less than 4.8 cb. ft. (300 litres per kg.) of gas per 1 lb. measured at a barometric pressure of 30 in. and a temperature of 60° F. (15.5° C.). Carbide of the above sizes yielding less than 4.8 cb. ft. per lb. shall be paid for in proportion to the gas yield—that is, the price to be paid shall bear the same relation to the contract price as the gas yield in cubic feet per 1 lb. bears to 4.8. A buyer may refuse to take carbide of standard size yielding less than 4.2 cb. ft. per 1 lb. (262 litres per kg.). A latitude of 5 per cent. is allowed in the analysis, and the actual gas yield is deemed to be that ascertained by the analyst plus 5 per cent.

According to F. B. Gatehouse,<sup>1</sup> the gas yield may be determined in any apparatus which permits an excess of water to act upon a known weight of carbide, and in which it is possible to measure the evolved gas accurately under standard conditions of temperature and pressure.

The regulations of the German Acetylene Union are as follows:—Commercial carbide of the standard size, lumps of 15 to 18 mm. diameter, should yield on an average 300 litres of crude acetylene at 15°C. and 760 mm. per 1 kg.; a latitude of 2 per cent. in the analysis is allowed. If the yield lies between 270 and 300 litres per 1 kg. (with a latitude of 2 per cent.), the carbide must be accepted by the buyer, but a proportional reduction in the price may be made. Carbide which yields less than 270 litres per 1 kg. may be rejected. All particles of the sample which pass through a sieve of 1 sq. mm. mesh is to be regarded as dust.

Fine-grain carbide, in pieces of from 4 to 15 mm. diameter should yield on an average 270 litres of crude acetylene per 1 kg., with a latitude of 2 per cent. in the analysis. If the yield lies between 250 and 270 litres per 1 kg., with a latitude of 2 per cent. in the analysis, the carbide must be accepted, a proportional reduction in price being allowed. Carbide which yields less than 250 litres per 1 kg. may be rejected.

The analyses must in all cases be conducted in accordance with the regulations prescribed by the Union.<sup>2</sup>

One kilogram of chemically pure calcium carbide yields 406.0 g. of pure acetylene, which at 0° C. and 760 mm. occupy 341.42 litres.<sup>3</sup>

The calculation of the observed volume of acetylene to 0° C. and

<sup>1</sup> *Acetylene*, 1909, 6, 57.

<sup>2</sup> Published by Marhold, Halle, 1900.

<sup>3</sup> *Note*.—The value 341.42 litres is based on the weight of the litre of acetylene as determined by experiment. The value calculated from the molecular volume per gram-molecule of 22.412 litres is 349.7 litres per 1 kg. calcium carbide.



760 mm. pressure is greatly facilitated by the use of the tables given in the Appendix to Vol. I. (Tables VI. and VII., pp. 921-932). The table (VI.) for the temperature reduction can be used even where the gas is to be reduced to 15° C. instead of 0° C. In this case the volume of gas found at  $t^\circ$  is taken from the column for 15°, and the volume reduced to 15° is found in the same horizontal line under the column  $t$ . For instance, if 16.5 litres of gas at 20° C. are obtained from 50 g. of calcium carbide, then, according to the table:—

15°	20°
16.12	15.84
17.06	16.76

A simple mental calculation shows that 16.5 in the first column corresponds sufficiently closely with 16.2 in the second, *i.e.*, that 16.5 litres at 20° would occupy 16.2 litres at 15°. The reduction can of course be also calculated by the formula:—

$$V_{15} = V_t \times \frac{273 + 15}{273 + t}$$

A table calculated by Hammerschmidt<sup>1</sup> facilitates the reduction of the gas volume to 15° C. and 760 mm. pressure for temperatures of from 0° to 30° C. and barometric pressures of 660 to 780 mm. The observed barometric pressure must be corrected for the temperature of the mercury (this is most simply done by subtracting 1 mm. for temperatures from 0° to 12°, 2 mm. from 13° to 19°, and 3 mm. for temperatures of 20° and upwards). The barometric pressure must also, of course, be corrected by subtracting the vapour tension of water for the temperature in question, as indicated in Table VIII. of the Appendix to Vol. I. (p. 933). Hammerschmidt further gives the following sufficiently accurate formula for the calculation:—

$$V_{15} = \frac{v}{100} (140.2 - 0.6t) \frac{B}{100},$$

in which  $V_{15}$  is the required volume at 15° C.,  $v$  the volume read at  $t^\circ$  C., and  $B$  the corrected barometric pressure.

In Great Britain it is not usual to correct the volume of gas for the tension of aqueous vapour, it being assumed that the volume required by the test is that which the user of the carbide may be expected to obtain easily in his own apparatus in ordinary use.

The relation of the percentage of calcium carbide to the yield of gas is shown in the following Table (p. 594), due to F. B. Gatehouse.<sup>2</sup> The data are given both in litres per kilogram at 15° C. and 760 mm., and in cubic feet per lb. at 60° F. and 30 ins.

<sup>1</sup> *Acetylen in Wissensch. und Industrie*, 4, 69.

<sup>2</sup> *Loc. cit.*

Table for the correction of the volume of Acetylene in cubic feet to 60° F. and 30 in. pressure.

Milli- metres.	Inches.	°C. 10. °F. 50.	°C. 11·1. °F. 52.	°C. 12·2. °F. 54.	°C. 13·3. °F. 56.	°C. 14·4. °F. 58.	°C. 15·5. °F. 60.	°C. 16·6. °F. 62.	°C. 17·7. °F. 64.	°C. 18·8. °F. 66.	°C. 20. °F. 68.	°C. 21·1. °F. 70.	°C. 22·2. °F. 72.	°C. 23·3. °F. 74.	°C. 24·4. °F. 76.
721·36	28·4	970	965	960	955	951	946	941	936	931	926	921	915	910	905
723·90	28·5	973	968	964	959	954	949	944	939	934	929	924	919	914	908
726·44	28·6	977	972	967	962	958	953	947	943	938	932	927	922	917	912
728·98	28·7	980	975	970	966	961	956	951	946	941	936	931	925	920	915
731·52	28·8	984	979	974	969	964	959	954	949	944	939	934	929	924	918
734·06	28·9	987	982	977	973	968	963	958	953	948	942	937	932	927	921
736·60	29·0	990	986	981	976	971	966	961	956	951	946	941	935	930	925
739·14	29·1	994	989	984	979	975	969	964	959	954	949	944	939	933	928
741·68	29·2	997	992	988	982	978	973	968	962	958	952	947	942	937	931
744·22	29·3	1001	996	991	986	981	976	971	966	961	956	950	945	940	935
746·76	29·4	1004	999	995	990	985	980	975	969	964	959	954	949	943	938
749·31	29·5	1008	1003	998	993	988	983	978	973	968	962	957	952	947	941
751·85	29·6	1011	1006	1001	996	992	986	981	970	971	966	960	955	950	944
754·39	29·7	1015	1010	1005	1000	995	990	985	980	974	969	964	959	953	948
757·13	29·8	1018	1013	1008	1003	998	993	988	983	978	972	967	962	957	951
759·67	29·9	1022	1017	1012	1007	1002	997	991	986	981	976	970	965	960	954
762·21	30·0	1025	1020	1015	1010	1005	1000	995	990	985	979	974	968	963	958
764·75	30·1	1029	1024	1019	1014	1009	1003	998	993	988	983	977	972	966	961
767·29	30·2	1032	1027	1022	1017	1012	1007	1002	996	991	986	980	975	970	964
770·83	30·3	1036	1030	1025	1020	1015	1010	1005	1000	995	989	984	978	973	968
773·37	30·4	1039	1034	1029	1024	1019	1014	1008	1003	998	993	987	982	976	971
775·91	30·5	1042	1037	1032	1027	1022	1017	1012	1006	1001	996	991	985	980	975
778·45	30·6	1046	1041	1036	1031	1026	1021	1016	1011	1005	1000	995	989	984	978
780·99	30·7	1049	1044	1039	1034	1029	1024	1019	1014	1009	1003	998	993	987	982
783·53	30·8	1053	1048	1043	1037	1032	1028	1023	1018	1013	1007	1002	997	991	985
786·07	30·9	1056	1051	1046	1041	1036	1031	1026	1021	1016	1010	1005	1001	995	989

F. B. Gatehouse<sup>1</sup> gives the preceding Table (p. 593), based on one published by Leeds & Butterfield, for the correction of the gas volume. The volume of gas found is multiplied by the factor in the Table and divided by 1000; this gives the value in cubic feet at 60° F. and 30 in. pressure:—

**Percentage of Calcium Carbide and corresponding Gas Yield of Acetylene.**

Calcium Carbide.	Acetylene.	Acetylene.	Calcium Carbide.	Acetylene.	Acetylene.	Calcium Carbide.	Acetylene.	Acetylene.
Per cent.	Litres per kg.	Cub. feet per lb.	Per cent.	Litres per kg.	Cub. feet per lb.	Per cent.	Litres per kg.	Cub. feet per lb.
100	365·62	5·862	90	329·12	5·272	80	292·62	4·682
99	361·97	5·803	89	325·47	5·213	79	288·97	4·623
98	358·32	5·745	88	321·82	5·154	78	285·32	4·564
97	354·67	5·685	87	318·17	5·095	77	281·67	4·505
96	351·02	5·626	86	314·52	5·036	76	278·02	4·446
95	347·37	5·567	85	310·87	4·977	75	274·67	4·387
94	343·72	5·508	84	307·22	4·918	74	271·02	4·328
93	340·07	5·449	83	303·57	4·859	73	267·37	4·269
92	336·52	5·390	82	299·92	4·800	72	263·72	4·210
91	332·77	5·331	81	296·27	4·741	71	260·07	4·151
						70	256·42	4·092

**Methods employed for the Determination of the Yield of Gas.**

A large number of methods and forms of apparatus have been proposed for this determination, of which the following are the most important:—

**1. Caro's Apparatus.**<sup>2</sup>—This apparatus (Fig. 81), which is used in many laboratories and carbide works, consists of a decomposition vessel, A, a washer, B, and a gas-holder, C. The decomposing vessel is cylindrical, with a slanting bottom, and is provided with an outlet for the residues, *a*, a gas exit-tube, *b*, and a screw-down lid, *b'*. The upper portion of the vessel is fitted with ten boxes for taking the carbide, which are so arranged round a central axis that they can be successively emptied into the water of the evolution apparatus by turning the crank *i* and tapping the bottoms of the cases. The washer B is provided with a thermometer. The gas-holder C is fitted with a scale and indicator, a manometer, *n*, and a control thermometer, *o*; the gas exit-tube is provided with a stopcock, *q*.

The gas-holder has a capacity of about 200 litres, the height of the bell is 850 mm., and the diameter 550 mm., and it is graduated so that the gas volume can be read to 0·5 litre. The capacity of each carbide holder is sufficient to hold 0·5 kg. with ease.

<sup>1</sup> *Acetylene*, 1909, 6, 56.

<sup>2</sup> Cf. Vogel, *Handbuch für Acetylene*, p. 106.



To carry out the estimation, the water in the gasometer is first saturated with acetylene by decomposing about 300 to 400 g. of any sample of carbide, the gas being kept for two hours under the pressure

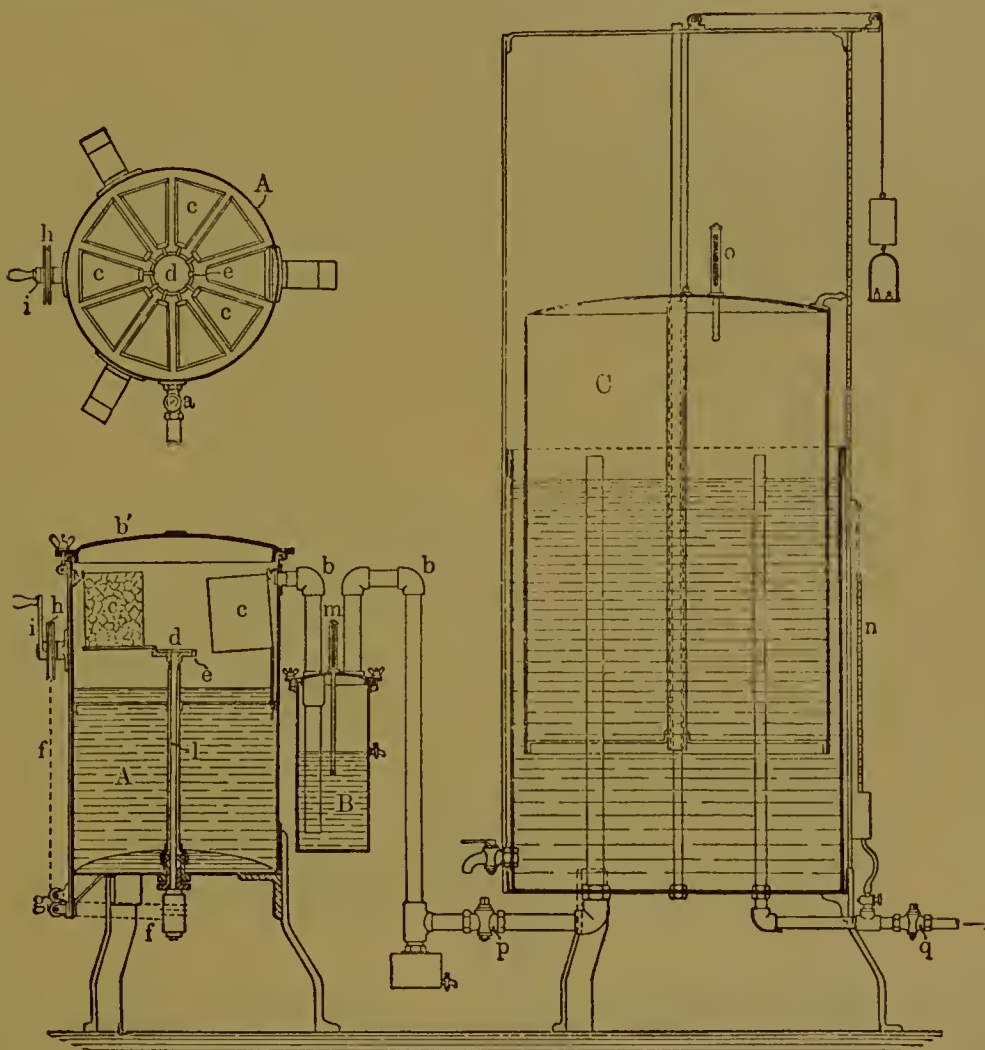


FIG. 81.

of the water in the gasometer; it is then allowed to escape, and the gasometer emptied to the zero point of the scale. The sample of carbide, weighed to within 0.5 g., is then distributed as evenly as possible amongst the ten decomposition vessels, the cover *b* screwed down, and the crank *i* turned so that the first portion of the carbide is decomposed. After waiting five to ten minutes until the bulk of the gas has been evolved, the stopcock *p* is closed, weights are placed on the ball of the gasometer until the manometer is brought to the zero, the height of the gasometer, the temperature, and the barometric pressure read, and the gasometer again emptied to the zero point. The connecting stopcock *p* is then opened, the contents of the second carbide holder transferred to the decomposing vessel by turning the

crank *i*, and so on until the whole of the sample has been decomposed. In decomposing the last portion it is necessary to wait for at least two hours before reading, in order to effect complete decomposition.

2. **J. W. Gatehouse's Apparatus.**<sup>1</sup>—This apparatus is shown in Fig. 82.

Two hundred and fifty grams of the carbide, crushed to about the size of walnuts, are placed in seven circular zinc trays, about 35 to 40 g. being placed in each. Each tray is divided by a vertical partition into two divisions, one being perforated at the bottom and the other near the top. The generator is provided with a drip-tap, *g*, and a tap, *h*, for running off the sludge. The trays are filled and placed as rapidly as

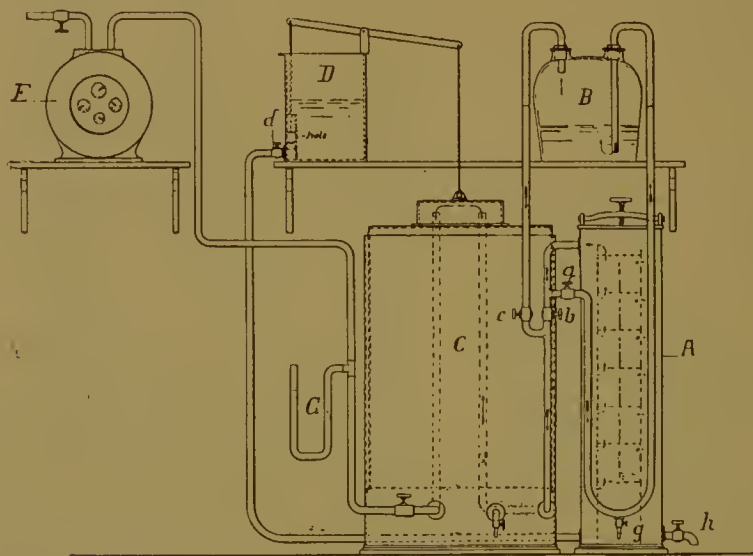


FIG. 82.

possible in the generating vessel A, and the lid screwed down. By turning tap *d*, water is allowed to run in from the reservoir D into the generator A, whence it enters the first carbide container, as indicated by the arrow, and acts upon the first portion of the carbide. The acetylene generated passes out through the tap *a* (the tap *b* being closed), into the wash-bottle B, which is charged with water saturated with acetylene, and thence through *c* to the gas-holder C, which floats in water saturated with acetylene and is fitted with a manometer, G, by means of which the working pressure may be ascertained; G also acts as a safety valve in case of obstruction in the gas pipes or meter. As the bell rises, the water supply is automatically cut off, so that only a small weight of carbide is acted upon by excess of water until the whole charge is decomposed. About 250 c.c. of water rise to each compartment, and the apparatus is so designed that each compartment

<sup>1</sup> *Acetylene*, 1909, 6, 56.

is flooded in turn, thus ensuring the necessary excess of water. From the gas-holder the gas passes to the meter E, fitted with a thermometer, where the gas volume is measured in litres; the volume is then corrected to the standard temperature and pressure. J. W. Gatehouse<sup>1</sup> considers this more satisfactory than the employment of a large gasometer, in which he finds it is difficult, under ordinary conditions, to maintain a sufficiently exact temperature. With proper sampling he finds the variations do not exceed  $\frac{1}{2}$  litre (say 0.7 per cent.).

**3. Lunge and Cedercreutz's Apparatus.**<sup>2</sup>—This consists of a sheet-metal cylinder open at the top and filled with water, in which a sheet-metal bell is suspended by pulleys and counterweights (Fig. 83). For the introduction of the gas, a tube may be led down to the bottom and bent round under the bell, or a short tube may be fixed into the cover of the bell, and connected with the apparatus in which the gas is evolved by a rubber tube, *a*, so that the bell can rise freely, as shown by the dotted lines. In either case, an outlet for the gas with a tap, *b*, is provided in the cover of the bell, the gas being driven out and burnt after the experiment. By means of a pointer, *d*, and a graduated scale, *c*, on one of the supports, the volume of gas evolved can be read off. A thermometer and manometer must be attached to the apparatus.

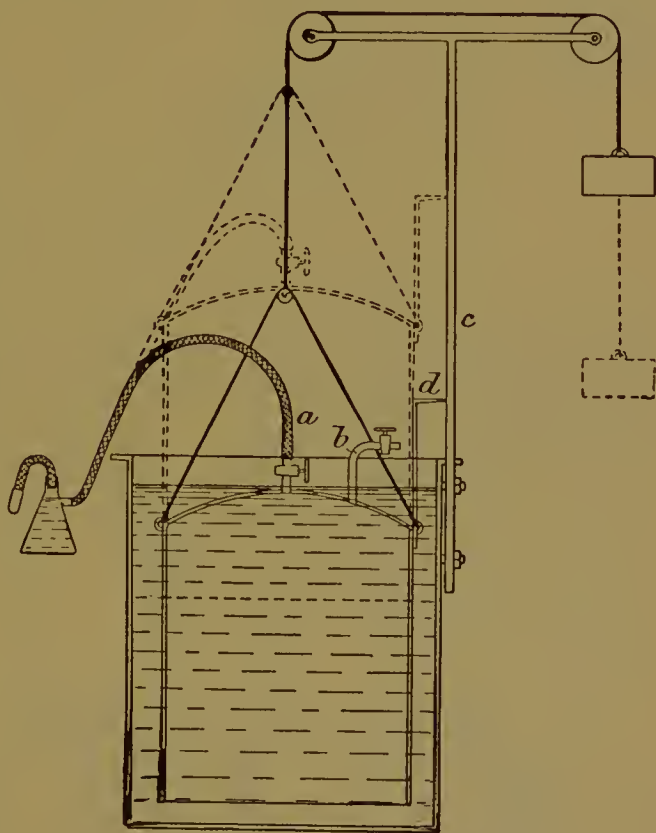


FIG. 83.

**4. Other Volumetric Methods.**—If no gasometer of this kind is available, the apparatus described in Vol. I., Fig. 144, p. 506, may be made use of, but for the examination of 50 g. of calcium carbide, the bottle must have a capacity of 20 litres. In this case, the water is alternately run into two graduated cylinders; the gas volume can then be very accurately measured in this way.

Instead of the graduated cylinder, a second bottle can, of course, be used, being connected with the first by a rubber tube, which is joined

<sup>1</sup> Private communication.—C. A. K.

<sup>2</sup> *Z. angew. Chem.*, 1897, 10, 651.



to a tube passing to the bottom of the bottle, as in H. Bamberger's<sup>1</sup> apparatus, Fig. 84; the raising and lowering of bottles of 20 litres capacity is, however, somewhat tedious. The exit tube from the decomposition vessel C is filled with cotton wool.

Since acetylene is somewhat readily soluble in water, pure water should never be used in the gasometer, but always water completely saturated with acetylene. This is most readily prepared by decomposing two portions of carbide, each 1 per cent. of the weight of the water, and allowing the gas to bubble through the water; or, a concentrated solution of common

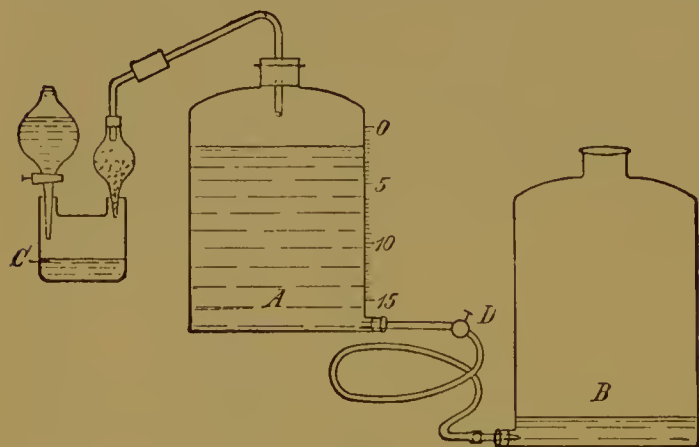


Fig. 84.

salt, which dissolves very little acetylene, may be employed, but even this must be treated once with the gas, if the apparatus is to be used for accurate measurements. It has also been suggested to cover the water with a thin layer of oil, but if the above conditions are observed, this is unnecessary. Apart from this, oil dissolves acetylene to some extent, as Fuchs and Schiff have shown, and is, therefore, better omitted.

For the decomposition of the calcium carbide two methods are available. The apparatus for one of these is shown in Fig. 85, the carbide being weighed into the flask, and the water being gradually allowed to flow in.

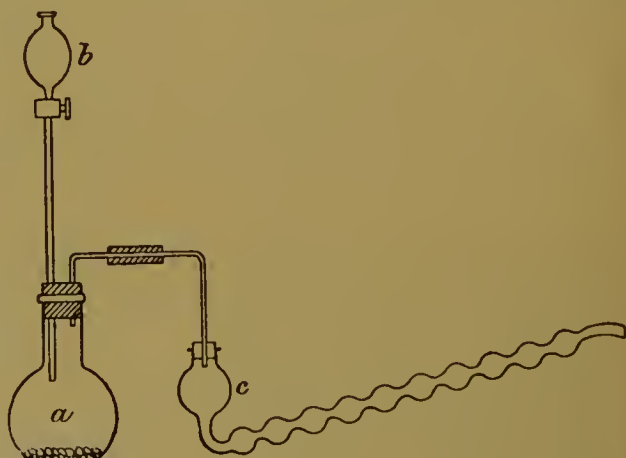


Fig. 85.

In the other method the process is reversed, the apparatus shown in Fig. 86 being used. The flask *a* is filled with a solution of common salt, the carbide weighed into the tube *b*, which is connected at once with the wide and thick rubber tube *c*, which must be dry, at any rate at the end connected with *b*. The carbide is then allowed to fall into the liquid by raising *c*. In order that the evolution of gas may not be too vigorous, it is advisable to attach a clip, *d*, and to

<sup>1</sup> *Z. angew. Chem.*, 1898, **11**, 242.

allow the carbide to fall into the flask *a* in several portions. In a few minutes the evolution of gas, the rate of which may be accelerated by shaking, is completed. The latter method has the advantage that it is unnecessary to dry the flask *a* carefully, for each experiment, as in the former method. The former, however, is more suitable, when it is desired, not to measure the gas, but to determine the impurities in it (cf. *infra*).

The following form of apparatus (Fig. 87), constructed of glass and in which not less than 50 g. of carbide is decomposed, has been designed in accordance with the specifications of the German Acetylene Union. It is advisable to decompose the carbide by allowing it to fall into water; if it be desired to allow the water to drop on to the carbide, the decomposition should occupy three to three and a half hours for 50 g. of carbide, and the gas must be measured with all the usual precautions.

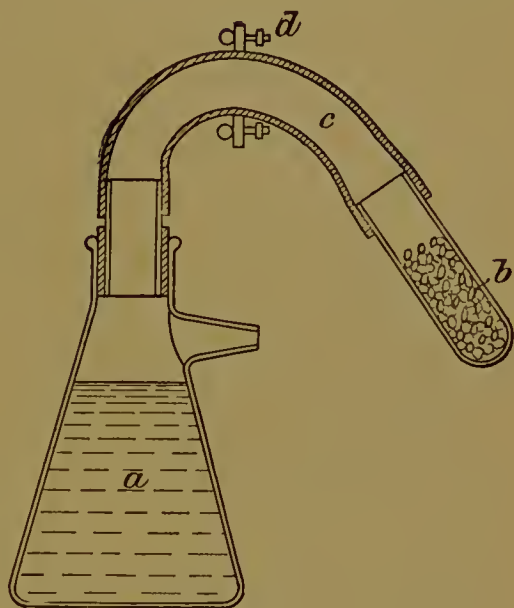


FIG. 86.

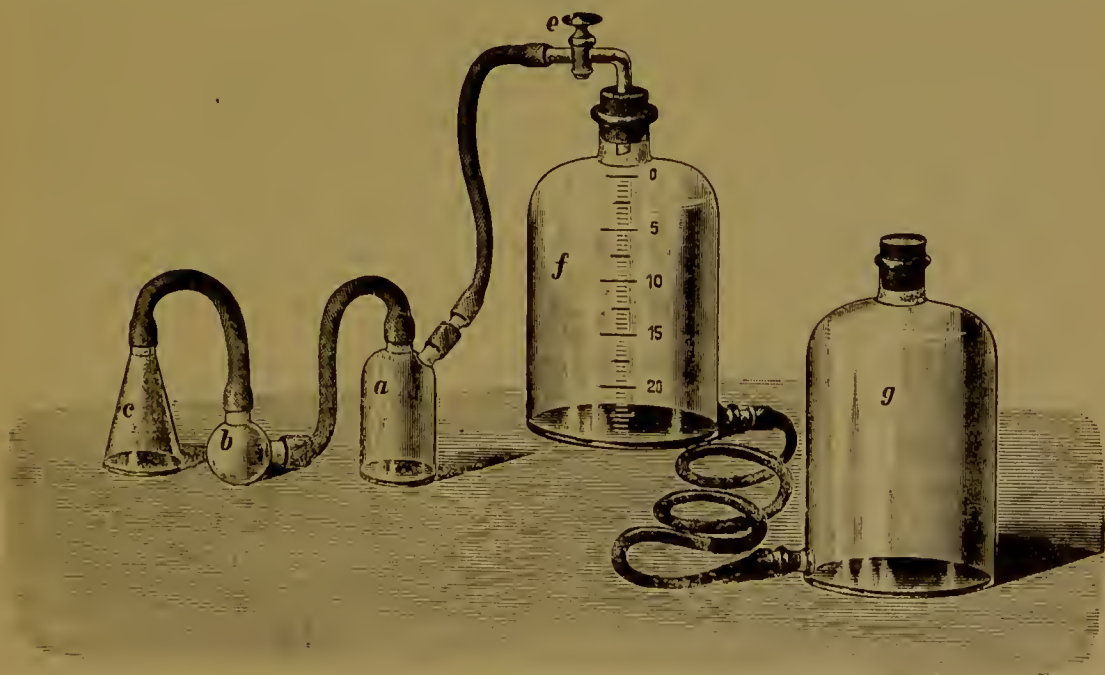


FIG. 87.

The carbide samples should be broken up in a dry, iron mortar with a leather or rubber cover, or in an apparatus similar to a coffee mill.

The decomposition vessel *a* has a capacity of about 250 c.c., the neck

is 15 mm. in diameter, and is connected by a piece of rubber tubing with the bulb *b*, which has two tubular outlets. This bulb is further connected with the conical flask *c*, of about 100 c.c. capacity; the bottle *a* is also connected, through the tap *e*, with the measuring flask *f*, of 20 litres capacity, which is filled with water saturated with acetylene and connected at the bottom with a bottle, *g*, of the same size. To carry out a determination, 150 c.c. of water saturated with acetylene are placed in the bottle *a*, the bottle *f* filled to the zero mark with water saturated with acetylene by raising *g*, the tap *e* closed, and the rubber tubes joined up between *a* and *e*. Fifty grams of carbide are then weighed into *c* and allowed to fall, little by little, into the bulb *b* and thence into *a*, the tap *e* having been previously opened and the bottle *f* raised somewhat. Finally, the apparatus is allowed to stand for two hours, the height of the water in *f* and *g* adjusted to the same level by raising or lowering the vessels, and the volume of the gas in *f* read, the temperature and barometric pressure being observed at the same time. In place of the combination *a*, *b*, *c*, a dropping arrangement similar to that shown in Fig. 85 may be used, about 150 g. of water being allowed to drop on to 50 g. of carbide in about three hours; heating must be avoided, if necessary, by immersing the apparatus in cold water.

Rossel and Landriset<sup>1</sup> have described an apparatus in which a perforated zinc basket, to hold 25 g. of carbide, is fastened to a glass rod, which can be pushed through the cork of a bottle of 6 to 7 litres capacity. The gas is liberated by lowering the basket into the water in the bottle (5 litres), and is passed through any desired number of wash-bottles, and then into a gasometer of 10 litres capacity, the bell of which is 10 cm. in diameter and very accurately graduated. The water used for decomposing the carbide must be previously saturated with acetylene by the introduction of two lots, of 30 g. each, of calcium carbide; the water of the gasometer is saturated with common salt. The gasometer is fitted with a water manometer and a thermometer. The rise of temperature is very different, according as the carbide is plunged completely or only superficially into the water, as is also the amount of sulphuretted hydrogen evolved. By dropping water on to the carbide considerable quantities of sulphuretted hydrogen and other sulphur compounds are liberated, whilst, by suddenly plunging the carbide into water, no sulphuretted hydrogen is evolved.

A very convenient form of apparatus has been described by Cedercreutz.<sup>2</sup>

The apparatus devised by Setterberg<sup>3</sup> is useless, as it is only available for 3 g. of calcium carbide. That of Magnanini and Vannini<sup>4</sup>

<sup>1</sup> *Z. angew. Chem.*, 1901, 14, 78.

<sup>2</sup> *Ibid.*, 1901, 14, 83.

<sup>3</sup> *Chem. Zeit. Rep.*, 1900, 24, 4.

<sup>4</sup> *Chem. Centr.*, 1900, I., 1308.



is not much better, being only adapted for 6 to 7 g.; such small samples can never give representative tests. The apparatus of Recchi<sup>1</sup> also offers no special advantage.

**5. Gravimetric Methods of Estimation.**—H. Bamberger's method (p. 598) was originally devised for the gravimetric valuation of calcium carbide.<sup>2</sup> The decomposition is effected in the flask A (Fig. 88) by the liquid from the dropping funnel B, the evolved gas passed through a calcium chloride tube, C, and the loss of weight of the whole apparatus, after the completion of the decomposition, determined. Pure calcium carbide gives 40 per cent. by weight of acetylene. A 15 to 20 per cent. solution of sodium chloride was employed for decomposing the carbide, and the addition carried out very slowly (about three to four hours), as in the apparatus for the measurement of the evolved gas. In both cases a salt solution should be used, firstly, because it dissolves very little acetylene, and secondly, because the amount of heat evolved is less than when pure water is employed.

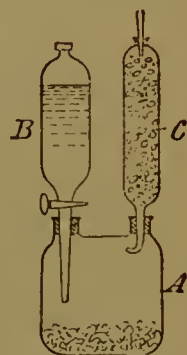


FIG. 88.

The loss of weight observed may be calculated either as percentage of  $\text{CaC}_2$  (0.406 g. loss of weight = 1 g.  $\text{CaC}_2$ ), or in litres of acetylene (341.42 litres  $\text{C}_2\text{H}_2$  at  $0^\circ$  and 760 mm. correspond to 1 kg.  $\text{CaC}_2$ . See *Note*, p. 591). Bamberger gives a table to facilitate the calculation.

Other forms of apparatus for the gravimetric valuation of carbide have been described by Erdmann and V. Unruh<sup>3</sup> and by Formenti.<sup>4</sup>

For accurate determinations, these gravimetric methods are not to be recommended, as only small quantities of carbide can be decomposed, and it cannot always be ensured that the gas evolved in the simple apparatus, such as must be used for the determinations, is completely dried, a consideration which holds also for the analogous determination of carbonic acid.

### The Complete Analysis of Calcium Carbide.

Complete analyses of calcium carbide are seldom carried out. According to Vogel,<sup>5</sup> they comprise the following determinations:—

1. Pure carbide. 2. Decomposable sulphur compounds. 3. Undecomposable sulphur compounds. 4. Decomposable phosphorus compounds. 5. Undecomposable phosphorus compounds. 6. Decomposable silicon compounds. 7. Undecomposable silicon compounds. 8. Free carbon. 9. Combined carbon. 10. Calcium carbonate. 11. Calcium oxide. 12. Iron and oxide of iron. 13. Magnesia. 14. Alumina. 15. Other constituents (nitrogen, etc.)

<sup>1</sup> *Chem. Centr.*, 1903, I., 1438.

<sup>3</sup> *J. prakt. Chem.*, 1901 [2], 64, 233.

<sup>2</sup> *Z. angew. Chem.*, 1898, II., 196.

<sup>4</sup> *Chem. Centr.*, 1902, II., 1341.

<sup>5</sup> *Handbuch für Acetylen*, p. 121.

The content of pure carbide is obtained from the estimation of the gas yield of crude acetylene, and the estimation of the contained compounds of phosphorus, sulphur, silicon, nitrogen, etc. The proportion of these products in the crude acetylene depends essentially upon the method of decomposition adopted; it is always less when a large excess of water is employed in the decomposition of the carbide than when an insufficient quantity is used, as in the dropping and dipping forms of apparatus.

The analysis of the undecomposed residue is conducted as follows:—The residue is slightly acidified with hydrochloric acid, the resulting solution filtered and made up to a definite volume. An aliquot portion of this solution is treated with hydrochloric acid, and a copper salt, and the contained sulphur thus precipitated as cupric sulphide; the sulphur thus estimated, together with that contained in the gas, gives the sulphide-sulphur of the total decomposable sulphur compounds. The remainder of the above solution is used for the estimation of silica, alumina, oxide of iron, and magnesia. The residue insoluble in hydrochloric acid is divided into two portions. One portion is used for the estimation of carbon (other than that present as calcium carbide) by combustion with chromic acid, and the other is fused with sodium carbonate and nitrate. The flux is extracted and evaporated with hydrochloric acid, the residual silica filtered off, and sulphuric acid, phosphoric acid, iron, alumina, calcium, and magnesium estimated in the filtrate. The undecomposable sulphur and phosphorus compounds and silica are thus determined.

According to Gall,<sup>1</sup> the sulphur remains in the milk of lime, when the carbide is decomposed by a large excess of water (as in the methods in which the carbide is dropped into the water), and may be determined in the residue as barium sulphate. He found, as a mean, 6.6 kg. in 1 ton of carbide. The phosphorus, on the other hand, passes completely into the gas. In order to determine the phosphorus, the powdered carbide is thrown into red-hot, molten sodium nitrate, in which it burns. The mass is dissolved in water, excess of nitric acid added, and the phosphoric acid determined by the molybdate method. Gall found up to 648 g. of phosphorus per 1 ton of carbide (0.065 per cent.), which was derived from the lime, the electrodes and the anthracite.

Lidholm<sup>2</sup> examined this method, but found it unsatisfactory. He also rejects Gall's method for the determination of the sulphur in calcium carbide as inaccurate, and recommends the following procedure, for the determination of the sulphur present, both as calcium sulphide and as aluminium sulphide. About 3 g. of powdered calcium carbide are mixed with five times the quantity of pure potassium

<sup>1</sup> *Z. Electrochem.*, 1903, 9, 772.

<sup>2</sup> *Z. angew. Chem.*, 1904, 17, 558.

sodium carbonate, which has been fused and subsequently powdered and 2 parts of anhydrous ammonium chloride, free from sulphur. The mixture is heated in a covered porcelain crucible with a powerful spirit lamp, the crucible being moved from side to side with the tongs. A gas-burner may also be used with safety, if the products of combustion are prevented from coming into contact with the contents of the crucible as described in Vol. I., p. 246. After the mixture has been kept liquid for five minutes, it is poured on to a slab of marble or other material, and after cooling, introduced into a flask provided with a tap-funnel and a reflux condenser. The condenser is connected with two Peligot tubes, containing a solution of cadmium and zinc acetates (5 g. cadmium acetate, 20 g. zinc acetate, and 200 c.c. glacial acetic acid, diluted to 1 litre with water). The air is displaced from the apparatus with carbon dioxide, 100 c.c. of water are allowed to flow in from the tap-funnel, and then 25 c.c. of hydrochloric acid of sp. gr. 1.19 added, drop by drop. The evolved gases (carbon dioxide and sulphuretted hydrogen) pass through the receivers, in which the sulphuretted hydrogen is retained. When the evolution of gas has ceased, the carbon dioxide generator and the condenser are connected up, and the liquid is boiled for about ten minutes to drive all the sulphuretted hydrogen into the receivers. The contents of the latter are then treated with 10 c.c. of a solution of 120 g. of crystallised copper sulphate and 120 g. of concentrated sulphuric acid in 1 litre, which converts the acetates to sulphates. The sulphides are thus converted to copper sulphide,<sup>1</sup> which is filtered and washed, heated and strongly ignited in a closed crucible, to convert it wholly to cupric oxide. The weight of the  $\text{CuO} \times 0.4030 =$  total sulphur in the carbide. Lidholm found 0.585 to 0.610 g. of sulphur per kilogram of carbide by this method.

Carbonates may be estimated by decomposing the carbide with water in an Erlenmeyer flask, liberating the carbon dioxide by the addition of phosphoric acid,<sup>2</sup> and then driving it over by means of a current of air into a receiver containing barium hydroxide.

### C. ACETYLENE

The ordinary impurities of technical acetylene have been summarised on p. 587. The majority of these are unimportant for practical purposes, especially as they occur only in very small quantities. Only phosphoretted hydrogen and volatile sulphur compounds are of importance, on account of the injurious action of their combustion products; for this reason they are frequently determined quantitatively. If the small quantities of other impurities ammonia, carbon monoxide,

<sup>1</sup> Cf. Classen, *Ausgewählte Methoden der anal. Chem.*, vol. i., p. 520.

<sup>2</sup> Vogel, *Handbuch für Acetylen*, p. 122.



hydrogen, nitrogen, oxygen (methane has never been detected with certainty) are to be determined, large quantities of the crude acetylene (about 500 c.c.) must be treated with fuming sulphuric acid, which absorbs the acetylene and ammonia, and the remaining gases examined by the ordinary gas analytical methods.

**1. Harmful Impurities.**—Keppeler<sup>1</sup> uses a solution of mercuric chloride in hydrochloric acid as a general reagent for the detection of harmful impurities in acetylene. Bergé and Reyckler had previously recommended this reagent, which gives a precipitate in presence of such impurities. The most convenient method is to use black filter paper soaked with mercuric chloride,<sup>2</sup> which is moistened with 10 per cent. hydrochloric acid solution, and held over an unignited acetylene burner. In presence of compounds of phosphorus, sulphur, or silicon, a white deposit is formed on the paper, whilst pure acetylene gives no deposit.

F. B. Gatehouse<sup>3</sup> recommends white paper soaked in an ammoniacal solution of silver nitrate as a general test for purity. With properly purified acetylene the paper will remain unchanged for at least half an hour; with impure gas it will become black in a few minutes.

Rossel and Landriset<sup>4</sup> analyse the acetylene in a Hempel burette of 100 c.c. capacity, filled with mercury. The acetylene is first absorbed in 30 c.c. of fuming sulphuric acid and subsequently the oxygen by alkaline pyrogallol, the hydrogen and methane determined by explosion, whilst the nitrogen is estimated by difference. This method is very inexact, as the quantity of the impurities amounts, according to the author's own results, to only 0.1 or 0.2 per cent. by volume and this small quantity must be transferred backwards and forwards several times from the burette to the pipettes.

Methods for the complete analysis of acetylene, which is practically never required for technical purposes, have been described by Haber and Oechelhäuser, v. Knorre and Arndt and Fränkel.<sup>5</sup>

**2. Phosphoretted hydrogen and Sulphuretted hydrogen.**—As stated above, these are the most important impurities to be determined in acetylene.

The limit for phosphoretted hydrogen prescribed by the British Acetylene Association is 0.05 per cent. by volume, or 0.075 g.  $\text{PH}_3$  per 100 litres of acetylene. The German Acetylene Union prescribes a limit of 0.04 per cent. by volume of phosphorus compounds, calculated as  $\text{PH}_3$ , with a permissible analytical error of  $\pm 0.01$  per cent.

Phosphoretted and sulphuretted hydrogen may be detected

<sup>1</sup> *J. Gasbeleucht.*, 1904, 47, 461.

<sup>2</sup> These papers can be obtained from E. Merck, Darmstadt.

<sup>3</sup> *Acetylene*, 1909, 6, 80.

<sup>4</sup> *Z. angew. Chem.*, 1901, 14, 77.

<sup>5</sup> Cf. Vogel, *Handbuch für Acetylen*, p. 247.

qualitatively by the known methods of gas analysis, but their quantities are so small that reliable results are seldom obtained, and it is, therefore, better to proceed direct to the quantitative examination.

The test for phosphoretted hydrogen (after removal of sulphuretted hydrogen) by silver nitrate, proposed by Eckelt, is very unreliable, as the silver nitrate may be reduced by other compounds.

The application of mercuric chloride is described on p. 604.

The first reliable quantitative method proposed is the following, due to Lunge and Cedercreutz<sup>1</sup>:—For the determination of the sulphur and phosphorus, as sulphuretted and phosphoretted hydrogen respectively, in the acetylene, the gas collected in the gasometer over water or salt solution must not be used, as the liquid always absorbs some of the impurity, but the gas must be passed direct from the generator through the absorption tubes employed. In using the apparatus of Bamberger (Fig. 88, p. 601) this may be combined with the determination of the acetylene by the loss of weight.

For the quantitative determination of the phosphoretted hydrogen, Willgerodt<sup>2</sup> proposed oxidation by bromine water, which is, however, inapplicable, on account of the strong action of bromine on acetylene itself. Lunge and Cedercreutz<sup>3</sup> have shown that the best reagent for this purpose is a solution of chloride of lime or sodium hypochlorite, the latter being the more convenient for analytical work. Both of these oxidise phosphoretted hydrogen easily and completely, whilst the hypochlorites are without action upon acetylene at ordinary temperatures. The sodium hypochlorite may be prepared by treating a solution of chloride of lime with sodium carbonate. The filtered solution absorbs phosphoretted hydrogen readily, and the resultant phosphoric acid may be precipitated directly from the solution by means of magnesia mixture. Lunge and Cedercreutz have shown that it is not necessary to decompose the hypochlorite previous to the precipitation.

To carry out the estimation, the apparatus shown in Fig. 85 (p. 598) is used; *a* is a well-dried 500 c.c. flask, into which 50 to 70 g. of the calcium carbide, broken into lumps of about the size of peas, are introduced. Finely divided carbide (dust) must not be used, firstly because it cannot be obtained without partial decomposition of the carbide, and secondly because it gives rise to a too vigorous evolution of gas. The carbide may be weighed directly in a tared flask, if a suitable balance is available; the balance should turn to 50 or at least 100 mg. A dropping funnel, *b*, fits into the neck of the flask, the lower end of the tube being drawn out to a capillary; the flask is connected with a ten-bulb absorption tube, *c*. As a further precaution, this tube may be connected

<sup>1</sup> *Z. angew. Chem.*, 1897, **10**, 651.

<sup>2</sup> *Ber.*, 1895, **28**, 2107.

<sup>3</sup> *Loc. cit.*

with a second ten-bulb tube, but this is unnecessary, if the prescribed conditions are adhered to. Seventy-five c.c. of a 2 to 3 per cent. solution of sodium hypochlorite are introduced into *c*, this quantity being sufficient for all cases likely to occur in practice. The dropping funnel is filled completely with water, and the rate of flow of water regulated to 6 to 7 drops per minute. The apparatus may be left to itself, as it is only necessary to add water to *b* from time to time and to shake the flask *a* gently. The evolution of gas is complete in three to four hours. Water is then allowed to flow into the flask until it is filled to the neck, and air aspirated through the apparatus in order to draw the gas in the large bulb of *c* through the smaller bulbs; the ten-bulb tube is then emptied into a beaker, rinsed out, and the phosphoric acid determined by magnesia mixture.

According to Keppeler,<sup>1</sup> explosions occasionally occur when acetylene is passed through solutions of sodium hypochlorite; this is true, but Lunge and Cedercreutz, after prolonged experience of the method, state that such explosions are extremely rare.

One per cent. by volume of  $\text{PH}_3$  corresponds to 14.0 g. P per cubic metre of acetylene.

One per cent. by volume of  $\text{SH}_2$  corresponds to 14.5 g. S per cubic metre acetylene.

In their analyses of various sorts of carbide, Lunge and Cedercreutz found between 0.0380 and 0.0750 g.  $\text{Ca}_3\text{P}_2$  per kg. carbide, corresponding to 93.1 to 184 c.c.  $\text{PH}_3$ , or, assuming the yield of gas to be 300 litres, 0.031 to 0.061 per cent.  $\text{PH}_3$  by volume.

According to Eitner and Keppeler,<sup>2</sup> this method is not quite accurate, since certain organic phosphorus compounds are present in the acetylene which are not converted to phosphoric acid by hypochlorite. They prefer, therefore, to burn the acetylene, rendering the flame non-luminous and free from soot by means of oxygen, in a special burner, under a glass hood. The hood is connected with two ten-bulb tubes and a Peligot receiver, and finally with a water suction-pump. The first ten-bulb tube contains water, the second a solution of sodium hypobromite prepared from sodium hydroxide and bromine; the last receiver is empty. The pump is regulated so that the air-bubbles in the ten-bulb tubes can just be counted; the height of flame is such that about 10 litres of acetylene are burnt per hour. A large portion of the phosphoric anhydride,  $\text{P}_2\text{O}_5$ , which results from the combustion, is deposited on the glass hood, which must, therefore, be well washed with water containing some hydrochloric acid. The solution thus obtained is evaporated with ammonium carbonate to remove the silica taken up from the glass. After filtering, this solution is added to that in the receivers and the phosphorus determined by the molybdate method,

<sup>1</sup> *J. Gasbeleucht.*, 1904, 47, 62.

<sup>2</sup> *Ibid.*, 1901, 44, 548.



and the sulphur in the filtrate as barium sulphate. More phosphorus is stated to be found in this way than by the hypochlorite method.

Keppeler<sup>1</sup> has shown that air may be used instead of oxygen, for the above combustion; the gases should then be passed through a ten-bulb tube, the first bulbs of which are filled with pieces of resistance glass, and the condensed water should be treated with bromine to oxidise the sulphur dioxide present.

According to Lidholm (cf. *infra*), this method suffers from the defect that the water or salt solution cannot be added to the carbide with sufficient regularity to ensure a steady current of gas to the burner without a regulator, and that a regulator, if used, might again give rise to errors.

According to Vogel,<sup>2</sup> N. Caro had previously worked out a method very similar to the above, and constructed a portable apparatus for the purpose.

Silicon compounds can also be determined in the gas by the combustion method, but the hood must in this case be made of platinum or nickel and the gas must be passed through perfectly pure sodium hydroxide (prepared from sodium), in which the silica is absorbed and determined by the usual method, after washing out the hood and adding bromine water. Phosphoric and sulphuric acids are determined in the filtrate.

J. W. Gatehouse<sup>3</sup> makes use of the combustion method employing the decomposition vessel used in determining the gas yield (Fig. 82, p. 596). The acetylene is burnt in an ordinary acetylene burner, at the rate of 10 litres per hour, under a glass bell-jar from which the combustion products pass by means of an adapter into the base of a drying jar. The upper part of the drying jar is fitted with a spiral or sinuous tube, surrounded by water, the lower end of which passes water-tight through the constriction in the body of the drying jar whilst the upper end is bent at an angle of about 45° and is continued for some length so as to act as a chimney. Water is allowed to drop into this tube during the whole period of combustion, some 300 c.c. being required in all. The combustion chamber is closed at the bottom by a glass, porcelain, or lead tray, having a hole in the centre for the passage of the burner. After the completion of the combustion, which with 250 g. of carbide requires some seven to eight hours, the apparatus is allowed to cool, after which the whole is well washed out, first with the water which has passed through the spiral tube and finally with distilled water; the total bulk of solution so obtained should be about 400 c.c. This acid liquid is then titrated with *N*/10 sodium hydroxide solution, employing phenolphthalein as indicator. The quantity of alkali required will vary,

<sup>1</sup> *J. Gasbeleucht.*, 1903, 46, 777.

<sup>2</sup> *Handbuch für Acetylen*, p. 243.

<sup>3</sup> *Acetylene*, 1908, 5, 167; 1909, 6, 58.

according to the quality of the carbide, from 20 c.c. to 100 c.c. per 100 litres of gas burnt; 1 c.c.  $N/10$  NaOH = 0.0017 g.  $\text{PH}_3$ . Should the quantity taken be less than 44 c.c. per 100 litres of gas burnt (which corresponds to 0.075 g.  $\text{PH}_3$  or 0.05 per cent. by volume, the limit fixed by the British Acetylene Association), it will be unnecessary to proceed further unless the actual amount of phosphorus in the gas has to be determined. In the latter case, the neutralised solution is treated with an excess of hydrochloric acid and evaporated to dryness, a few drops of nitric acid being added towards the end, to render any silica present insoluble, and to completely oxidise all phosphorus compounds to phosphates. The residue is redissolved in dilute acid and the phosphorus in solution estimated as magnesium pyrophosphate. The sulphuric acid may be estimated in the filtrate if the magnesia mixture has been prepared from pure magnesium chloride.

Lidholm<sup>1</sup> also makes use of the evolution of acetylene from the carbide, but effects this, by the addition of alcohol, so slowly that the gas may be passed into the burner without first passing through a gas regulator. The last portions of the gas are displaced by hydrogen. For this purpose he uses a decomposition flask of 500 c.c. capacity with a reflux condenser, which is also provided with a dropping funnel and a tube for the admission of the hydrogen. From the reflux condenser, the gas passes into a small acetylene burner, above which stands a glass cylinder 32 cm. long and 5 cm. wide, open at the bottom, and connected at its upper end with a wash-bottle and then with a filter pump. About 10 g. of carbide are introduced in a crucible, at the bottom of the flask, the air displaced with hydrogen, which is ignited, and the filter pump set in action. Fifty c.c. of anhydrous alcohol are then allowed to flow on to the carbide, and then the same quantity of water. The acetylene evolved burns, and the phosphoric acid formed is collected, partly in the cylinder and partly in the wash-bottle. When the evolution of gas is complete, hydrochloric acid is poured into the flask to dissolve the lime, and so minimise the risk of the flask breaking on heating, and the liquid is heated to boiling point, the current of hydrogen being allowed to pass continuously through the flask; the cylinder, connecting tubes, and receiver are then rinsed out with warm, dilute ammonia, the solution filtered from the silicic acid which is generally formed, and the phosphoric acid precipitated with magnesia mixture.

According to Hempel and Kahl,<sup>2</sup> phosphoretted hydrogen in acetylene can be easily and quickly determined as follows:—The gas is measured in a burette filled with mercury, and then driven over into a gas pipette containing mercury and 3 c.c. of copper sulphate solution (prepared from 15.6 g. of crystallised copper sulphate, 100 c.c. of water,

<sup>1</sup> *Z. angew. Chem.*, 1904, **17**, 1452; cf. also Henrichsen, *Chem. Centr.*, 1907, **II.**, 1356.

<sup>2</sup> *Z. angew. Chem.*, 1898, **11**, 53.

and 5 c.c. of dilute sulphuric acid (1:5), the solution being previously saturated with acetylene). The contents of the pipette are shaken for three minutes, and the unabsorbed gas measured. A quarter of the diminution in volume thus found corresponds to the phosphoretted hydrogen. This method, like others depending on the measurement of the residual gas, has several disadvantages. Firstly, errors may result from the decomposition of phosphoretted hydrogen by oxygen dissolved in the water, as mentioned by the authors themselves; secondly, an objection which is crucial for the practical application of the method, is that the traces of phosphoretted hydrogen present in the acetylene cannot be measured with any certainty, as the pipettes hold only 100 c.c., and the phosphoretted hydrogen only amounts to a few hundredths of a cubic centimetre.

Sulphur occurs in technical acetylene, not only as sulphuretted hydrogen (which is by no means completely retained, notwithstanding the strongly alkaline reaction of the residue), but also in other combinations, as has been proved by Lunge and Cedercreutz, Moissan, and many others.

These sulphur compounds are oxidised by the hypochlorite solution to sulphuric acid, and may be estimated by barium chloride in the acidified filtrate from the phosphorus determination, if the hypochlorite solution and magnesia mixture are free from sulphates. A simpler plan, however, is to divide the hypochlorite solution into two parts, and to use one for the estimation of the phosphoric acid, and the other for that of the sulphuric acid.

**3. Ammonia.**—This occurs in barely estimable quantities only. For its determination the gases are passed through acid, and the absorbed ammonia subsequently estimated by "Nesslerising" (*cf.* Vol. I., p. 766). The titration of the excess of acid is inapplicable, owing to the minute proportions of ammonia present.

**4. Heat of Decomposition.**—In addition to the determination of the gas yield, and the estimation of the harmful impurities, the heat of decomposition is now receiving some attention.<sup>1</sup> Undue heating frequently follows the use of an unsuitable generator, but it appears also to be sometimes associated with impurities in the carbide. Considerable help is afforded on this point by an examination of the sludge left after decomposition, which should be white from a pure carbide properly decomposed, but assumes a yellow or black tinge when insufficient water has been used. That different makes of carbide may give widely varying heats of decomposition is indicated by the great variations in the rate of gas evolution published in the 1908 Report of the Technological Museum, Vienna,<sup>2</sup> according to which samples yielding in all, in ninety minutes, 316.62, 281.08, and 278.40 litres of gas per kilo-

<sup>1</sup> *Cf.* Gatehouse, *Acetylene*, 1908, 5, 346.

<sup>2</sup> *Ibid.*, 1909, 6, 280.



gram gave, in the first two minutes, 180, 68, and 38 litres respectively. Gatehouse<sup>1</sup> has described a simple apparatus which allows of comparable results being obtained, and serves to eliminate any carbide likely to cause excessive heat in practice. The apparatus is arranged as follows:—A calcium chloride drying tower is fitted at the neck with a two-holed cork, carrying a thermometer and a leading tube. The side hole at the base of the tower is also fitted with a cork provided with a glass tube and stopcock, which is connected to a graduated reservoir. Fifty grams of the carbide to be tested are placed in the main body of the tower, the cork inserted so that the thermometer rests just above the surface of the carbide, sufficient water then added just to fill the base of the tower without coming into contact with the carbide, and the temperature noted. A measured excess of water, say 75 c.c., is then run in to decompose the carbide, the thermometer carefully watched, and the highest temperature reached recorded; this should not exceed 100°.

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<sup>1</sup> *Acetylene*, 1909, 56, 6.

END OF PART I.



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